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CXV.—ON NITROMALONIC ALDEHYDE.

BY HENRY B. HILL AND JOSEPH TORREY, JR.

INTRODUCTION.

BY HENRY B. HILL.

In 1882 Hill and Sanger[1] published a preliminary notice describing briefly certain bodies which they had obtained by the action of alkaline nitrites upon mucobromic acid and its esters. When an alcoholic solution of mucobromic acid was added to a solution of potassic nitrite in diluted alcohol, reaction soon set in, the solution became deep-red, carbonic dioxide was evolved, and, as the solution cooled, an orange-red potassium salt separated which had the formula $K_2C_3HN_2O_3$. While this salt was quite stable in alkaline solution, and could readily be recrystallized from warm water on the addition of a small quantity of potassic hydrate, it was rapidly decomposed when heated in neutral aqueous solution; a complicated reaction set in, in which carbonic dioxide was evolved, hydrocyanic acid formed, and at the same time a colorless potassium salt, which crystallized in well-formed prisms as the solution cooled; this colorless salt was shown to have the formula $KC_3H_2NO_4.H_2O$. With sodic nitrite the reaction proved to be similar, except that in this case no deeply colored intermediate compound could be isolated; the main product formed was a colorless sodium salt which had the composition $NaC_3H_2NO_4.H_2O$, and corresponded to the color-

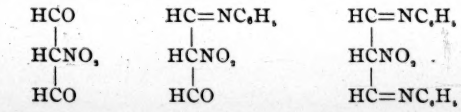
[1] Ber. d. chem. Ges., 15, 1906.

less potassium salt already obtained. With ethyl mucobromate a reaction of entirely different character took place; in this case no carbonic dioxide was formed, while the bromine was completely removed, and if potassic nitrite was used, a sparingly soluble, highly crystalline, and stable salt was formed which had the formula $KC_5H_4NO_6$. The mode of formation and the behavior of these three sets of salts warranted the conclusion that they all contained the nitro group, but no facts were discovered which threw further light upon their constitution. From the sodium salt, $NaC_5H_3NO_4.H_2O$, a number of other salts were made by double decomposition, and while these salts were not especially stable, no suspicion was entertained at the time that they were not salts of a nitro acid of ordinary type. The study of these bodies was unavoidably interrupted soon after the publication of this preliminary note, and on account of the press of other work the subject received no further attention for many years. Although the negative results which Hill and Sanger had obtained made the outlook appear rather unpromising, Dr. Torrey was interested several years ago to continue the investigation with me, and a brief note containing some of our results has already appeared.[1]

We chose as our starting point the colorless salt which is apparently the final product of the action of alkaline nitrites upon mucobromic acid in alcoholic solution. A study of this, the most stable, and at the same time the most simple body formed in the reaction, could hardly fail to give a clue to the structure of the more complicated products. Since the sodium salt is more easily and economically prepared than the potassium salt, we have used it in all our work. We found at the outset that we could get no well-defined derivatives either by reduction or oxidation, and that the free acid could not be isolated from aqueous solution by the ordinary methods. On the addition of aniline hydrochlorate to an aqueous solution of the sodium salt, a bright yellow, highly crystalline compound was soon formed, which could readily be recrystallized from alcohol. This body proved to have the formula $C_9H_8N_2O_3$, so that an atom of oxygen in the body $C_5H_4NO_4$, from which the

[1] Ber. d. chem. Ges., **28**, 2597.

sodium salt is derived, had been removed and replaced by the phenylimido group. While this body was not further attacked by aniline hydrochlorate, aniline readily removed a second atom of oxygen and formed the body $C_{13}H_{12}N_2O_2$. The latter compound could be made more easily by the direct action of aniline dissolved in diluted alcohol upon the sodium salt. The formation of these two aniline derivatives by the successive replacement of oxygen by the group C_6H_5N rendered it extremely probable that the sodium salt itself contained two aldehyde groups:

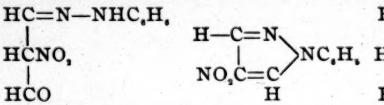


With *p*-toluidine the analogous derivatives were easily obtained, and methylamine, ethylamine, or isoamylamine also formed similar compounds. As might have been expected, we obtained with phenylhydrazine bodies which were precisely analogous to the aniline derivatives; their isolation required more care, however, since they were easily decomposed with the formation of a substituted pyrazol, while we had been unable to convert the aniline derivatives into a substituted quinoline, the formation of which from *β*-diketones under similar conditions had previously been observed.[1] When phenylhydrazine hydrochlorate was added to an aqueous solution of the sodium salt a yellow hydrazone soon separated in clustered prisms, while phenylhydrazine itself gave under the same conditions finely felted needles of the sodium salt of the dihydrazone. This sodium salt was decomposed even by carbonic dioxide with the liberation of a brilliant red dihydrazone. When either of these two phenylhydrazones is dissolved in boiling alcohol, a substance crystallizes as the solution cools which has the composition of a phenylnitropyrazol. This well-crystallized and remarkably stable body gave in unmistakable fashion the pyrazol reaction described by Knorr,[2] when it was reduced in alcoholic solution by

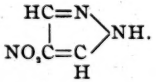
[1] Ber. d. chem. Ges., **20**, 1767; **28**, 1038; Compt. rend., **106**, 142.

[2] Ann. Chem. (Liebig), **238**, 200.

sodium, and the product oxidized with potassic dichromate after acidification with sulphuric acid. This behavior of the sodium salt toward phenylhydrazine, since it is identical with that shown by β-diketones and keto-aldehydes of known structure, was sufficient to establish it as a derivative of nitromalonic aldehyde :



Since the phenylnitropyrazol thus prepared had not previously been described, and its structure was therefore to a certain extent a matter of conjecture, it seemed of interest to prepare by the action of hydrazine the corresponding nitropyrazol. This body was first made by Buchner and Fritsch,[1] and its constitution was later established by Hantzsch,[2] who showed that it contained its nitro group upon the central carbon atom. We have made no extended study of the products formed by the action of hydrazine upon the sodium nitromalonic aldehyde, but we have shown that a nitropyrazol is readily formed through a secondary reaction, and that this product is evidently identical with the 4-nitropyrazol of Buchner.



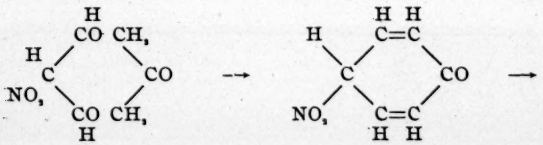
Hydroxylamine reacts promptly in alkaline and neutral solution with sodium nitromalonic aldehyde, but we have had great difficulty in obtaining satisfactory results in the study of the products formed. If hydroxylamine hydrochlorate is added to a concentrated aqueous solution of the salt, a colorless, neutral body is thrown down, which from its composition and its neutral character must be considered as the β-nitroisoxazol, corresponding to the bodies described by Claisen[3] and his pupils as formed under similar conditions from β-dike-

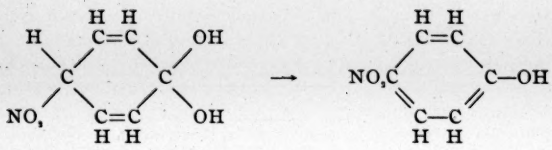
[1] Ann. Chem. (Liebig), **273**, 265.
[2] *Ibid.*, **279**, 228.
[3] Ber. d. chem. Ges., **21**, 1149 ; **21**, 2178 ; **24**, 130 ; **24**, 3900.

tones and keto-aldehydes. With free hydroxylamine in concentrated aqueous solution the sodium salt of a dioxime is formed, but the dioxime itself seems incapable of separate existence. On careful acidification of this sodium salt, a complex reaction ensues which is at present under investigation. A more complete description of the derivatives of both these oximes must be reserved for a subsequent paper.

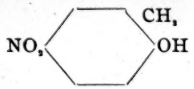
The whole behavior of the sodium salt in question is, therefore, in accordance with the supposition that it is a derivative of nitromalonic aldehyde. The question of the position of the sodium atom did not at first interest us directly, since this is evidently the same as that in the analogous salts of the nitroparaffins. Later we attempted to obtain evidence upon this point, but our experiments had been brought to no satisfactory conclusion when other investigations upon the same subject appeared, and we have not carried them farther.

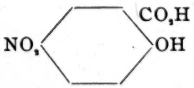
In order to show still more conclusively that our substance was a double aldehyde, it seemed advisable to involve both aldehyde groups simultaneously in a typical reaction of condensation. It is evident that such an aldehyde should condense with acetone, and that a six-carbon ring should be formed, if both methyl groups were attacked at the same time. Experiment showed that the reaction ran neatly and that in alkaline solution *p*-nitrophenol was formed in satisfactory quantity. The 1-nitro-4-keto-$\Delta_{2,5}$-dihydrobenzol which must be considered to be the first product of the condensation, evidently passes into the *p*-nitrophenol through the addition and elimination of water. The reaction is essentially the same whether the sodium nitromalonic aldehyde is assumed to be the nitro or the isonitro compound, and recalls the removal of the para hydrogens in $\Delta_{2,5}$-dihydrobenzol derivatives by oxidation, as observed by Von Baeyer; or the relation between quinonemonoxime and *p*-nitrosobenzol.

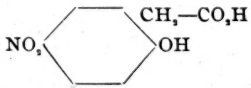




This reaction has been further studied by Messrs. G. Oenslager and C. A. Soch, who have found that a number of ketones and ketone-acids condense readily with nitromalonic aldehyde. From methyl-ethylketone was obtained the nitro-orthocresol of Nevile and Winther[1] melting at 95° while dibenzylketone yielded a nitrophenol derived from *m*-diphenylbenzol. The long-known nitrosalicylic acid melting at 228° was obtained from acetacetic ester, and a derivative of oxyphenylacetic acid of similar structure was made without difficulty from levulinic acid; acetonedicarboxylic acid also gave a nitrooxyisophthalic acid. The mode of condensation was sufficiently confirmed by the formation of the nitrocresol and the nitrosalicylic acid of known constitution, and the several products formed were therefore:







In attempting to prepare the free nitromalonic aldehyde from its sodium salt, we obtained results which confirmed in a striking way our conclusions as to the constitution of the body. When 1 molecule of hydrochloric acid was added to an aqueous solution of the sodium salt, no visible change took

[1] Ber. d. chem. Ges., 15, 2978.

place except a slight change of color, but after the lapse of a short time at ordinary temperatures, or more rapidly at a gentle heat, a beautifully crystalline body separated which proved to be symmetrical trinitrobenzol; at the same time formic acid appeared in the solution. It seems probable that the trinitrobenzol is here formed by the spontaneous condensation of nitroacetaldehyde, which is first formed together with formic acid by the addition of water to the nitromalonic aldehyde. The reaction is then precisely analogous to the formation of triacetylbenzol from acetoacetic aldehyde, or of trimesinic acid from malonic aldehyde acid. It is to be noted, however, that the condensation of the similar derivatives of acetaldehyde containing halogens with the formation of the corresponding derivatives of benzol has not been observed, and that it is not impossible, in this case, that the ring formation precedes the elimination of formic acid.

Nitromalonic Aldehyde.

The sodium salt of nitromalonic aldehyde and its salts with certain other bases were described in 1882 by C. R. Sanger in the preliminary paper already mentioned. As no analytic data were then given, we have thought it best to give here a more extended account of the preparation of the sodium salt which we employed, and to include also the analytical work of Sanger, through which its composition was established.

Sodium Nitromalonic Aldehyde, $NaC_3H_2NO_4.H_2O$.—When mucobromic acid is added to a solution of sodic nitrite in diluted alcohol a vigorous reaction soon sets in, the solution turns deep yellow, then deep red, and at the same time there is a rapid escape of carbonic dioxide. The temperature rises rapidly, and the reaction seems to proceed to best advantage at about 50°. We have usually dissolved 20 grams of sodic nitrite in 50 cc. of water, diluted the solution with an equal volume of alcohol, and then stirred in 20 grams of mucobromic acid. The temperature was allowed to rise spontaneously until it reached 50°. Cooling was seldom necessary to keep it at this point, and, as the reaction slackened, gentle heat was required. As soon as the evolution of carbonic dioxide is over, the solution should be well cooled and vigorously

stirred; the solution then solidifies with the separation of finely-felted needles of the sodium salt. The yield is usually 25 per cent of the weight of the mucobromic acid taken, but occasionally it has fallen considerably lower without our being able to fix upon the cause. The crude product is most conveniently purified by recrystallization from somewhat diluted alcohol. The air-dried salt contains 1 molecule of water, which it retains over sulphuric acid; at 100° slow decomposition sets in, so that a direct determination of the water of crystallization is impracticable.

I. 0.5188 gram air-dried salt gave 0.2325 gram Na_2SO_4.

II. 0.5837 gram air-dried salt gave 0.2238 gram Na_2SO_4.

III. 0.2742 gram air-dried salt gave 0.1240 gram Na_2SO_4.

IV. 0.5639 gram air-dried salt gave 0.4788 gram CO_2, and 0.1372 gram H_2O.

V. 0.6526 gram air-dried salt gave 0.5346 gram CO_2, and 0.1617 gram H_2O.

VI. 0.5739 gram air-dried salt gave 0.4883 gram CO_2, and 0.1438 gram H_2O.

VII. 0.5346 gram air-dried salt gave 43.0 cc. moist nitrogen at 26°.5 and under a pressure of 757 mm.

VIII. 0.7758 gram air-dried salt gave 63.5 cc. moist nitrogen at 18°.5 and under a pressure of 750 mm.

	Calculated for $NaC_3H_2NO_4.H_2O$.	Found.							
		I.	II.	III	IV.	V.	VI.	VII.	VIII.
Na	14.67	14.53	14.41	14.67	....	....	....	....	....
C	22.92	....	....	....	23.16	22.35	23.20	....	....
H	2.56	....	....	....	2.72	2.77	2.77	....	....
N	8.94	....	....	....	....	....	....	8.82	9.26

Sodium nitromalonic aldehyde is very readily soluble in water, but quite sparingly soluble in alcohol; from a hot alcoholic solution it is deposited in long, slender needles. It is not easy to obtain a perfectly colorless salt, although the color appears to be accidental. By treatment with bone-black and repeated recrystallization from alcohol, or by precipitation of the cold alcoholic solution with ether, a white salt may be prepared, but it still gives an aqueous solution, which is faintly tinged with yellow. The material which we have used throughout our work has had a decided reddish-yellow color.

Hill and Sanger did not succeed in isolating the aldehyde itself from the sodium salt, but they made no very persistent efforts in this direction. If an aqueous solution of the salt is acidified with hydrochloric acid and extracted with ether, the ether leaves upon evaporation a viscous oil which usually shows no signs of crystallization on standing. This ethereal extract, however, can easily be shown to contain the aldehyde, since the aniline derivative of the nitromalonic aldehyde melting at 143°–144°, which we shall soon describe, can readily be made from it. The oil dissolves in water, giving a brilliant yellow, clear solution, but this soon grows turbid and deposits a crystalline body which melts, after one recrystallization from alcohol, at 120°–121°. This same crystalline body can be prepared more conveniently by acidifying the solution of the sodium salt with exactly 1 molecule of hydrochloric acid and allowing it to stand. It is formed rapidly at 45°–50°, more slowly, but in somewhat better yield, at ordinary temperatures, while at 0° the formation is extremely slow; at 100° the reaction seems to take, in great part at least, another course. The body was readily soluble in alcohol, ether, chloroform, benzol, and ligroin, but was sparingly soluble even in boiling water. Repeated recrystallization from neutral solvents failed to raise the melting-point above 120°–121°, but after treatment with fuming nitric acid it melted at 121°–122°. This melting-point and the percentage composition of the body identified it as *s*-trinitrobenzol.

I. 0.2676 gram substance gave 0.3334 gram CO_2, and 0.0378 gram H_2O.

II. 0.1008 gram substance gave 17.5 cc. moist nitrogen at 21° and under a pressure of 764 mm.

	Calculated for $C_6H_3(NO_2)_3$.	Found. I.	II.
C	33.78	33.98	....
H	1.42	1.58	....
N	19.76	....	19.79

The body was further identified as *s*-trinitrobenzol through the formation of the characteristic addition-products with benzol and aniline described by Hepp.[1] By dissolving the sodium

[1] Ann. Chem. (Liebig), **215**, 356, 376.

nitromalonic aldehyde directly in half-normal hydrochloric acid we obtained from 20 to 24 per cent of the theoretical yield of trinitrobenzol, assuming that 3 molecules of the former were needed to form 1 molecule of the latter. A very slight excess of acid diminished the yield greatly; with 2 molecules of acid of this strength hardly any trinitrobenzol was formed.

The aqueous solution filtered from the trinitrobenzol proved to contain formic acid in abundance. It was distilled in a current of steam as long as acid was carried over; the acid distillate was boiled with an excess of plumbic carbonate, and the filtered solution concentrated. The lead salt thus obtained had the characteristic appearance of plumbic formate and gave the required percentage of lead.

0.3513 gram of the salt gave 0.3581 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	69.61

In aqueous solution, therefore, nitromalonic aldehyde is decomposed according to the equation:

$$3C_3H_3NO_4 = C_6H_3(NO_2)_3 + 3CH_2O_2.$$

If water is carefully excluded, the nitromalonic aldehyde may be isolated, but its preparation and purification is a matter of some difficulty. If an ethereal solution of hydrochloric acid is added to the silver salt suspended in absolute ether, argentic chloride is at once formed, and the ethereal solution, upon evaporation *in vacuo*, leaves a white crystalline residue, which may be recrystallized from ligroin or from a mixture of ether and ligroin. The analysis of a carefully prepared specimen gave figures which left no doubt as to the identity of the substance, but showed that decomposition had probably already set in.

0.1440 gram substance gave 0.1671 gram CO_2, and 0.0302 gram H_2O.

	Calculated for $C_3H_3NO_4$.	Found.
C	30.80	31.65
H	2.56	2.36

In order to determine whether the aldehyde had gone over into a polymeric form, its molecular weight was determined

through the depression of the freezing-point of its benzol solution. 25.1 grams of benzol were employed with the following results:

Substance.	Depression.	Molecular weight.
0.1206	0.200	117.7
0.1299	0.215	118.0

Since these results agree absolutely with the molecular weight 117, calculated from the formula $C_3H_3NO_4$, the substance was the monomolecular form of the aldehyde.

Nitromalonic aldehyde is readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble even in boiling ligroin. It may be most conveniently recrystallized from ligroin with the addition of a little ether, and is then obtained in feather-formed aggregations of small, pointed, colorless prisms which melt at 50°–51°. Water dissolves it immediately in the cold, giving an intensely yellow solution which is strongly acid toward litmus or methyl orange. The aqueous solution soon grows turbid with the formation of trinitrobenzol. With aniline it gives the crystalline aniline derivative already mentioned, melting at 143°–144°, and with sodic hydrate it forms the long needles of the sodium salt. It volatilizes rapidly when exposed to the air or even in a desiccator.

Action of Aniline and p-Toluidine.

Nitromalonic Aldehyde Anil, $C_9H_8N_2O_3$.—When aniline hydrochlorate is added to an aqueous solution of the sodic nitromalonic aldehyde, either with or without the addition of free hydrochloric acid, a highly crystalline, bright yellow substance is formed in abundance, which may be purified by recrystallization from alcohol. Analysis showed that it had been formed by the condensation of equal molecules of aniline and the aldehyde with the elimination of water.

I. 0.2202 gram substance gave 0.4543 gram CO_2, and 0.0864 gram H_2O.

II. 0.2453 gram substance gave 0.5045 gram CO_2, and 0.0965 gram H_2O.

III. 0.1202 gram substance gave 15.2 cc. moist nitrogen at 15° and under a pressure of 765 mm.

	Calculated for $C_9H_8N_2O_3$.	Found. I.	II.	III.
C	56.22	56.28	56.10	....
H	4.20	4.39	4.40	....
N	14.62	....	....	14.84

This substance is sparingly soluble in ether, chloroform, benzol, or ligroin, and insoluble in water. It dissolves freely in hot alcohol and crystallizes, as the solution cools, in irregular, lustrous, yellow scales, which melt at 143°–144°. In concentrated sulphuric acid it dissolves readily in the cold and is reprecipitated unchanged on the addition of water. The alkaline hydrates dissolve it at once in the cold, but ether then extracts aniline, and a salt of the aldehyde can be isolated from the solution.

Nitromalonic Aldehyde Dianil, $C_{15}H_{13}N_3O_2$.—If aniline is added to a solution of the sodium salt in water or diluted alcohol, a body is soon thrown down which crystallizes in brilliant yellow needles, while the solution acquires a strongly alkaline reaction. The same body may also be made by the action of aniline in alcoholic solution upon the anil which has just been described. For analysis the substance was recrystallized from dilute alcohol.

I. 0.1716 gram substance gave 0.4224 gram CO_2, and 0.0768 gram H_2O.

II. 0.1494 gram substance gave 19.5 cc. moist nitrogen at 7°.5 and under a pressure of 767 mm.

	Calculated for $C_{15}H_{13}N_3O_2$.	Found. I.	II.
C	67.36	67.14	....
H	4.90	5.01	....
N	15.77	....	15.86

The dianil is more readily soluble in alcohol, ether, chloroform, benzol, or ligroin than the compound with 1 molecule of aniline. As the method of preparation shows, it is little affected by dilute alkaline hydrates, but dilute acids readily convert it into the monoanil. When recrystallized from diluted alcohol it melts at 93°–94°.

Nitromalonic Aldehyde p-Tolil, $C_{10}H_{10}N_2O_3$.—This body is precipitated almost immediately when *p*-toluidine hydrochlorate is added to an aqueous solution of the sodium nitroma-

lonic aldehyde. It closely resembles the corresponding aniline compound in appearance and behavior. When recrystallized from alcohol it melts at 176°–177°.

0.2130 gram substance gave 0.4563 gram CO_2, and 0.0971 gram H_2O.

	Calculated for $C_{10}H_{10}N_2O_3$.	Found.
C	58.21	58.43
H	4.89	5.10

Nitromalonic Aldehyde Di-p-Tolil, $C_{17}H_{17}N_3O_3$.—The ditolil can be made by the action of 2 molecules of toluidine in alcoholic solution upon the sodium salt or upon the monotolil. It closely resembles the dianil, although it is rather more sparingly soluble in the ordinary solvents. When recrystallized from diluted alcohol it melts at 138°. Its composition was established by the following analyses:

I. 0.2071 gram substance gave 0.5278 gram CO_2, and 0.1087 gram H_2O.

II. 0.1590 gram substance gave 19.6 cc. moist nitrogen at 19°.5 and under a pressure of 772 mm.

	Calculated for $C_{17}H_{17}N_3O_3$.	Found. I.	Found. II.
C	69.10	69.52	....
H	5.80	5.87	....
N	14.27	....	14.30

Orthotoluidine gives similar compounds, but they have not been more fully studied. With methylamine, ethylamine, and isoamylamine, bodies may also be obtained which involve 1 or 2 molecules of the amine, and which closely resemble in behavior the aromatic compounds just described.

Action of Phenylhydrazine and of Hydrazine.

The behavior of the nitromalonic aldehyde toward phenylhydrazine demanded careful study, since the formation of pyrazol derivatives might be predicted. We have found that the phenylhydrazones are easily formed, and that they are also readily converted into phenylnitropyrazol.

Nitromalonic Aldehyde Phenylhydrazone, $C_9H_9N_3O_2$.—When 1 molecule of phenylhydrazine hydrochlorate is added to an aqueous solution of sodic nitromalonic aldehyde the hydra-

zone is soon formed and separates in short, clustered, yellow needles. As the substance could not be recrystallized without danger of decomposition, it was thoroughly washed with cold water, and dried at ordinary temperature. The dried substance had darkened materially in color, and it was therefore washed with a little cold alcohol and again dried. It then gave results on analysis which showed that it was the monohydrazone.

0.2332 gram substance gave 0.4474 gram CO_2, and 0.0958 gram H_2O.

	Calculated for $C_9H_8N_2O_3$.	Found.
C	52.13	52.32
H	4.38	4.59

This hydrazone is slightly soluble in water, and but sparingly soluble in cold ether or alcohol; it dissolves more freely in hot alcohol, and, if the solution is immediately cooled, small quantities may be recrystallized unchanged. On heating for a few minutes in alcoholic solution, it is converted into phenylnitropyrazol melting at 125°–126°; the same change is effected even in the cold on long standing. In hot benzol or chloroform the body dissolves freely, more sparingly in the cold; in carbonic disulphide it is sparingly soluble. On heating the substance melts at about 101°, but again solidifies and melts for a second time at 125°. This ready conversion by heat into the phenylnitropyrazol renders the precise determination of the melting-point impossible. It dissolves readily in dilute sodic hydrate, and phenylhydrazine hydrochlorate yields with this solution the sodium salt of the dihydrazone.

Nitromalonic Aldehyde Diphenylhydrazone, $C_{15}H_{14}N_4O_2$.—Phenylhydrazine dissolved in diluted alcohol reacts upon sodium nitromalonic aldehyde with the elimination of 2 atoms of oxygen; but since the dihydrazone thus formed is held in solution as a sodium salt, the deep-orange color which the solution soon assumes is the only indication that reaction has taken place. If an acid is now added, a voluminous precipitate of the dihydrazone is thrown down. Since the body is broken up by strong acids with the formation of phenylnitropyrazol, it is better to pass carbonic dioxide into the solution.

An orange-red precipitate at first appears, which grows compact and turns deep-red. As the substance could not be purified by recrystallization, it was washed thoroughly with cold water and carbonic disulphide, and dried over sulphuric acid.

I. 0.1388 gram substance gave 0.3080 gram CO_2 and 0.0649 gram H_2O.

II. 0.1410 gram substance gave 30.0 cc. moist nitrogen at 25° and under a pressure of 761 mm.

	Calculated for $C_{15}H_{18}N_8O_2$.	Found. I.	II.
C	60.54	60.52	....
H	5.08	5.23	....
N	23.61	....	23.94

The dihydrazone is insoluble in water and sparingly soluble in ether, chloroform, carbonic disulphide, benzol, ligroin, or cold alcohol; in hot alcohol it dissolves more freely, but as the solution cools phenylnitropyrazol separates. The formation of the pyrazol derivative is naturally facilitated by the addition of hydrochloric acid. In acetone the body dissolves freely, and is precipitated by the addition of chloroform or carbonic disulphide in a crystalline condition, but the crystals are soon converted into a viscous black mass. By the spontaneous evaporation of the ethereal solution small, deep-red, rhombic plates appear, but no considerable quantities of these crystals could be obtained without decomposition. The body melts at about 98° with decomposition. In alkaline solutions the dihydrazone dissolves freely and forms quite stable salts.

Sodium Nitromalonic Diphenylhydrazone, $NaC_{15}H_{14}N_4O_2$.— If the dihydrazone is dissolved in the requisite amount of half-normal sodic hydrate, the solution soon solidifies on scratching, with the separation of long, finely-felted, yellow needles of the sodium salt. This salt may also be made directly from the sodium nitromalonic aldehyde by the action of an aqueous solution of phenylhydrazine, or from the monohydrazone as already described. The salt is readily soluble in alcohol, sparingly soluble in cold water, more readily in hot, and may be recrystallized from water, if the solution is not too strongly heated.

I. 0.2794 gram salt gave 0.0626 gram Na_2SO_4.

II. 0.1872 gram salt gave 35.5 cc. nitrogen at 22°.5 under a pressure of 764 mm.

	Calculated for $NaC_{18}H_{14}N_4O_3$.	Found. I.	II.
Na	21.99	21.42	....
N	7.22	....	7.27

Lead Nitromalonic Diphenylhydrazone, $Pb(C_{18}H_{14}N_4O_3)_2$.—The yellow-brown lead salt made by double decomposition from the sodium salt was insoluble in water or alcohol.

0.1191 gram of the salt gave 0.0457 gram $PbSO_4$.

	Calculated for $Pb(C_{18}H_{14}N_4O_3)_2$.	Found.
Pb	25.87	26.20

1-Phenyl-4-Nitropyrazol, $C_9H_7N_3O_2$.—The formation of a phenylnitropyrazol from both the phenylhydrazine derivatives of the nitromalonic aldehyde by heating with alcohol has already been mentioned. When recrystallized from alcohol it gave the required percentage composition. The material used in analyses I and III was prepared from the monohydrazone; that used in analysis II was made by the action of dilute hydrochloric acid upon the dihydrazone.

I. 0.2104 gram substance gave 0.4392 gram CO_2, and 0.0732 gram H_2O.

II. 0.2595 gram substance gave 0.5431 gram CO_2, and 0.0908 gram H_2O.

III. 0.1380 gram substance gave 27.2 cc. moist nitrogen at 24°.5 and under a pressure of 765 mm.

	Calculated for $C_9H_7N_3O_2$.	Found. I.	II.	III.
C	57.09	56.96	57.09	....
H	3.73	3.89	3.91	....
N	22.26	....	....	22.10

The 1-phenyl-4-nitropyrazol is readily soluble in ether, chloroform, or benzol, but more sparingly soluble in ligroin. It dissolves readily in hot alcohol and, as the solution cools, it separates in slender clustered prisms, which melt at 126°–127°. It is not easy to remove the accidental color by recrystallization from alcohol, but from ligroin or ether the substance is readily obtained in nearly white, silky needles. It

gives without difficulty Knorr's pyrazol reaction. On diluting the alcoholic solution after reduction with sodium, a white crystalline product is thrown down which we have not further examined. While this body had the well-marked character of a pyrazol derivative, it had not previously been described, and it seemed advisable to prepare in a similar way from the nitromalonic aldehyde the 4-nitropyrazol which was first made by Buchner; such a body could evidently be made with the aid of hydrazine.

4-Nitropyrazol, $C_3H_3N_3O_2$.—Hydrazine sulphate gives with an aqueous solution of sodium nitromalonic aldehyde an immediate dark-red precipitate and a similar precipitate is also formed, if one equivalent of sodic carbonate or hydrate is added at the same time; if two equivalents of sodic hydrate are used, a yellow solution is obtained which is slowly precipitated by carbonic dioxide. The dark-red body thrown down in each case proved to be insoluble in all ordinary solvents, and appeared to be analogous to the phenyl compounds already studied. As they interested us mainly in that they might yield the nitropyrazol, we proceeded at once to a study of their decomposition. The product formed by the action of 2 molecules of the hydrazine sulphate with the addition of one equivalent of sodic carbonate proved to be much more stable than the phenylhydrazones. It was little affected by boiling water or alcohol, but when heated with dilute acids it slowly went into solution. On heating with moderately concentrated hydrochloric acid, the decomposition was more rapid; frequently complete solution was soon effected, but occasionally brown-red flocks were formed which resisted the action of the acid. The colorless solution was neutralized with sodic carbonate and extracted with ether. The ethereal solution left on evaporation a white crystalline solid, which was sparingly soluble in cold water, more readily in hot water, readily soluble in alcohol or ether, but sparingly soluble in benzol. It could be most readily purified by recrystallization from dilute alcohol; it could also easily be sublimed between watch-glasses. The recrystallized or resublimed body showed the constant melting-point 157°–158° (162° corrected), and agreed in its properties with the some-

what scanty description of nitropyrazol given by Buchner.[1] For the melting-point of the nitropyrazol Buchner gives 162°, but he does not say whether this is the corrected or the uncorrected temperature. Like the pyrazol of Buchner, this body gives with ammoniacal argentic nitrate a remarkably stable silver derivative. An analysis showed that the substance contained the proper percentage of nitrogen.

0.1146 gram substance gave 37.4 cc. moist nitrogen at 22°.8 and under a pressure of 765 mm.

	Calculated for $C_3H_3N_3O_2$.	Found.
N	37.23	36.92

From the red hydrazine derivative of the nitromalonic aldehyde, therefore, the 4-nitropyrazol is formed by the action of hydrochloric acid. In one case the weight of substance with the proper melting-point amounted to 65 per cent of the theoretical amount. It should be said that a small additional quantity of the nitropyrazol can be extracted by ether from the original mother-liquor from which the dark-red hydrazine compound has been removed by filtration.

Action of Hydroxylamine.

The action of hydroxylamine upon the nitromalonic aldehyde is closely analogous to that of the aromatic amines or hydrazines. In neutral solution hydroxylamine hydrochlorate gives a body which is empirically an anhydride of the monoxime, while in alkaline solution 2 molecules of hydroxylamine enter into reaction, and a salt of the dioxime is formed. The ready decomposition of these bodies has rendered the detailed study of them difficult; a more extended investigation of them is now in progress.

β-Nitroisoxazol, $C_3H_2N_2O_3$.—If 1 molecule of hydroxylamine hydrochlorate is added to a concentrated aqueous solution of sodic nitromalonic aldehyde, a deep-red color is soon developed, and on standing a white crystalline body separates. The same crystalline body is almost immediately obtained in larger quantity, if the hydroxylamine hydrochlorate is added in excess; in this case, however, a yellow instead of a red solution is formed. The crystals which separate

[1] Ann. Chem. (Liebig), 273, 265.

may be purified by recrystallization from ligroin, or from a mixture of ether and ligroin. Analysis showed that the body had been formed from the monoxime by the loss of a molecule of water.

I. 0.2290 gram substance gave 0.2630 gram CO_2, and 0.0375 gram H_2O.

II. 0.2078 gram substance gave 44.8 cc. nitrogen measured over caustic potash at 24° and under a pressure of 763 mm.

	Calculated for $C_3H_3N_3O_3$.	Found. I.	Found. II.
C	31.56	31.33	....
H	1.77	1.83	....
N	24.62	....	24.61

β-Nitroisoxazol is readily soluble in alcohol, ether, benzol, chloroform, sparingly soluble in cold carbonic disulphide, but more readily in hot, and very sparingly soluble even in boiling ligroin. It dissolves sparingly in cold water and gives a colorless solution which is neutral to litmus. The aqueous solution, on standing in the cold, gradually turns yellow and acquires an acid reaction; the same change takes place rapidly on warming. In solutions of the alkaline hydrates it dissolves promptly with the formation of a deep-yellow color; with sodic hydrate ammonia is given off in the cold and hydrocyanic acid is at the same time formed. From the acidified solution ether extracts no well-defined product. When crystallized from a mixture of ether and ligroin it forms clear rhombic plates, which are usually compactly aggregated, and show the constant melting-point, 46°–47°.

Sodium Salt of Nitromalonic Aldehyde Dioxime, $NaC_3H_4N_3O_4$. —When hydroxylamine hydrochlorate is allowed to act in concentrated aqueous solution upon sodium nitromalonic aldehyde with the addition of an equivalent amount of sodic carbonate or sodic hydrate, a sodium salt of the corresponding dioxime gradually separates as a pale-yellow, crystalline precipitate. The salt is rather sparingly soluble in cold water, and the solubility is somewhat increased by heat, but decomposition then soon sets in, and at 100° ammonia and hydrocyanic acid are formed. Evaporation in a desiccator gave us no satisfactory results, and the salt could not be precipitated from aqueous solution by alcohol. We therefore

analyzed the carefully prepared salt without further purification.

I. 0.1896 gram air-dried salt gave 0.0814 gram Na_2SO_4.

II. 0.1555 gram air-dried salt gave 33.2 cc. moist nitrogen at 18°.5 and under a pressure of 759 mm.

	Calculated for $NaC_3H_4N_3O_4$.	Found. I.	Found. II.
Na	13.61	13.92	....
N	24.90	....	24.45

This sodium salt crystallizes in clear, yellow, pointed prisms, which are frequently developed in the form of six-sided plates. If sodic hydrate is added to the salt suspended in cold water, it dissolves promptly, and alcohol then precipitates a new sodium salt which has not been further examined. On the addition of hydrochloric acid a complicated reaction takes place, which is at present under investigation, but as yet we have been unable to isolate the dioxime itself. The sodium salt gives with ferric salts a brown-red, with ferrous salts an intense blood-red color, which passes into an equally intense violet on the addition of sodic hydrate; if no large excess of ferrous salt is used, this alkaline solution is clear.

Silver Salt of Nitromalonic Aldehyde Dioxime, $AgC_3H_4N_3O_4$.—The pale-yellow, microcrystalline silver salt was at once precipitated on the addition of argentic nitrate to a solution of the sodium salt, and was not blackened by exposure to diffused light.

0.1000 gram salt gave 0.0566 gram AgCl.

	Calculated for $AgC_3H_4N_3O_4$.	Found.
Ag	42.47	42.60

Nitromalonic Aldehyde Anil-oxime, $C_9H_9N_3O_4$.—If aniline hydrochlorate is added to a solution of the sodium salt of the dioxime, a brilliant yellow, crystalline precipitate is at once thrown down, which can easily be purified by recrystallization from alcohol. Analysis showed that the body had been formed by the replacement of one of the isonitroso groups of the oxime by the phenylimido group.

I. 0.2421 gram substance gave 0.4636 gram CO_2, and 0.0978 gram H_2O.

II. 0.2272 gram substance gave 0.4340 gram CO_2, and 0.0912 gram H_2O.

III. 0.1175 gram substance gave 26.0 cc. moist nitrogen at 18° and under a pressure of 761 mm.

	Calculated for $C_3H_3N_3O_3$.	Found. I.	II.	III.
C	52.12	52.24	52.11	....
H	4.38	4.52	4.50	....
N	20.32	....	....	20.12

This anil-oxime is readily soluble in hot alcohol, and as the solution cools it separates in globular aggregations of yellow crystals which melt at 162°. It is but sparingly soluble in ether, chloroform, or benzol. It dissolves easily in dilute sodic hydrate, and is reprecipitated unchanged by acids. This body may also be made by the action of hydroxylamine upon the nitromalonic aldehyde anil melting at 143°–144°.

Condensation with Acetone.

If sodium nitromalonic aldehyde is dissolved in a small quantity of water, acetone in excess added, and the solution then made alkaline with sodic hydrate, a red color is soon developed which deepens as the solution stands. After the lapse of several hours, solid sodic hydrate is gradually added, and the yellow sodium salt which then separates recrystallized from water. The product which was obtained in this way, when acidified with hydrochloric acid, gave a body crystallizing in long, yellow needles, which melted at 114°. This melting-point and the properties of the substance were sufficient to show that it was *p*-nitrophenol, and the identity of the body was further established by an analysis.

0.1907 gram substance gave 0.3631 gram CO_2, and 0.0650 gram H_2O.

	Calculated for $C_6H_5NO_3$.	Found.
C	51.77	51.93
H	3.62	3.81

In alkaline solution, therefore, the nitromalonic aldehyde and acetone had condensed to form *p*-nitrophenol according to the equation :

$$C_3H_3NO_4 + C_3H_6O = C_6H_5NO_3 + 2H_2O.$$

Similar condensation-products formed from nitromalonic aldehyde by the action of other ketones and ketone acids will be described in a subsequent paper.

CONTRIBUTION TO THE STUDY OF AQUEOUS SOLUTIONS OF DOUBLE SALTS.

III.—CHLORIDES AND BROMIDES.

By Harry C. Jones and Nicholas Knight.

The purpose of this investigation is to study the condition of double chlorides and bromides in the presence of varying amounts of water. These substances are perfectly well-defined compounds, having a composition as definite, and a crystal form as characteristic, as any group of chemical substances.

The question is still unanswered as to the way in which these substances break down in aqueous solution. Are they first decomposed into their constituent molecules, and then these molecules dissociated electrolytically by the water, just as a mixture of the two substances would be, or do the molecules of the double halides exist as such in aqueous solutions, under any conditions?

Considerable work has already been done on this problem. Rüdorff[1] studied the way in which the constituents of double salts diffuse out of a solution of the salt, and divided double salts into two classes, according as their constituents were found in the diffusate in the same proportion as in the double salt, or in a different proportion. The following six double chlorides were found to suffer decomposition in the presence of water:

$2KCl + CuCl_2 + 2H_2O$,
$KCl + MgCl_2 + 6H_2O$,
$2NH_4Cl + CuCl_2 + 2H_2O$,
$2NaCl + CdCl_2 + 3H_2O$,
$2KCl + ZnCl_2 + H_2O$,
$BaCl_2 + CdCl_2 + 4H_2O$.

[1] Ber. d. chem. Ges., **21**, 4, 1882, 3044.

The following three double chlorides existed as such in the presence of water :

$$2NaCl + PtCl_4 + 8H_2O,$$
$$2KCl + PtCl_4,$$
$$2NH_4Cl + HgCl_2.$$

The first class, according to Rüdorff, are to be regarded as double salts, the second as true molecular binary compounds.

Berthelot,[1] from his thermochemical studies, laid down the general proposition that, " double salts formed with the liberation of a small amount of heat are to be regarded as separated, for the most part, into their constituents, by water." From his work on the double halides of potassium and mercury, he was led to conclude that double salts containing these substances are capable of existing in solution.

Since chemical changes are known to be accompanied by changes in volume, Kremers,[2] finding no change in volume when solutions of salts capable of forming double salts were mixed, concluded that no double salt existed in solution. Groshans,[3] from observations on double chlorides and sulphates, drew the same conclusion.

Grotrian[4] studied the conductivity of the double iodide of potassium and cadmium, and concluded that it was very nearly the sum of the conductivities of the constituents.

The application of the conductivity method to the problem of the existence of double chlorides in solution, has already been made by Jones and Ota.[5] They determined the conductivity of solutions of the double salts :

$$2KCl.ZnCl_2,$$
$$KCl.CdCl_2,$$
$$NaCl.AlCl_3,$$
$$2NH_4Cl.HgCl_2,$$

and then the conductivity of solutions of the constituents, in each case. They then compared the sum of the conductivities of the constituents, with the conductivity of the double

[1] Ann. chim. phys. [5], **29**, 198. [2] Ann. Phys. (Pogg.), **98**, 58.
[3] Des Dissolutions aqueuses, 2-7. [4] Ann. Phys. (Wied.), **18**, 177.
[5] This JOURNAL, **22**, 5.

salt at the same dilution, and finding that the conductivity of the double salt was always very much less than the sum of the constituents in concentrated solutions, concluded that in such solutions the double salt is only partly broken down into the constituent substances. As the dilution increased, the differences became smaller and finally vanished, showing that in very dilute solutions the double salt was entirely decomposed into its constituents.

We have extended the work which was begun on the double chlorides by Jones and Mackay,[1] and continued by Jones and Ota,[2] to a number of chlorides and bromides, and the results which we have obtained and our conclusions from them are given in this paper. The method of work is essentially the same as that employed by Jones and Ota. The conductivity of the double chloride was studied at various dilutions, then the conductivities of the constituent chlorides at the same dilutions, and the comparisons made as already described.

DOUBLE CHLORIDES.

The compounds of this class which we have studied are:

$2NaCl.ZnCl_2.3H_2O$,
$SrCl_2.2CdCl_2.7H_2O$,
$NH_4Cl.MgCl_2.6H_2O$,
$KCl.MgCl_2.6H_2O$.

The Double Chloride of Sodium and Zinc, $2NaCl.ZnCl_2.3H_2O$.

The sodium chloride and zinc chloride were brought together in the proportion of two equivalents of the former to one of the latter. The double salt crystallizes best when there is a slight excess of zinc chloride present. When an attempt was made to recrystallize the double salt, some sodium chloride first separated. Then the double salt readily crystallized. The double salt crystallizes in thick columns, and we were not able to obtain it in the form of needles, as described in the literature. The salt is deliquescent. Analysis gave the following results:

	Calculated.	Found.
H_2O	17.6	17.9

[1] This JOURNAL, **19**, 83. [2] *Ibid.*, **22**, 5.

The zinc in the anhydrous salt was then determined and found to be 25.24 per cent, while the calculated is 25.7 per cent. The solutions of this and of all the following salts were prepared thus: The salt was dissolved in water to approximately the concentration desired. This mother-solution was then standardized by determining some one of the constituents, the one chosen being that which could be most accurately and readily determined. Solutions 2 to 6, and in some cases 2 to 7, were each prepared directly from the mother-solution, by measuring off the desired volume of this solution into a measuring-flask, and then diluting to the required volume. Solutions 6 to 7, and in some cases 7 to 11, were prepared either from 6 or from 7 directly, in the same manner. Then No. 11 was taken as the mother-solution, and the remaining solutions prepared in a similar manner from it. In this way we avoided the accumulative effect of the errors of dilution which result whenever a given solution is diluted a large number of times. Duplicates of every dilution were made and their conductivities determined. All pipettes and measuring flasks used in this work were carefully calibrated by the method of Morse and Blalock.[1] In measuring the conductivity of the solutions two cells were used; one with the electrodes removed some distance from one another for the more concentrated solutions, and the other with the plates close together for the more dilute solutions. This was both more convenient and accurate than to use one cell for all of the dilutions. In this way considerable resistance could be used in the rheostat, even in the most concentrated solutions, and better minima secured; and further, by using the plates close together in the more dilute solutions, the resistance in the rheostat was not so great as to destroy the accuracy of the method.

We used the Ostwald modification of the Kohlrausch method. Two series of conductivity measurements were made, the solutions in each series being prepared separately.

Both cells were carefully standardized with $\frac{n}{50}$ potassium chloride ($\mu_v = 129.7$ at 25°), at the beginning of each series

[1] This JOURNAL, 16, 479.

of measurements for every substance employed. All the conductivity measurements were made at 25°.

In many cases the most dilute solution with which the wide electrodes were used was placed also in the cell with the electrodes close together, and thus its conductivity determined in both cells. This gave us an extra check on the standardization of both cells.

In the following tables v is the volume of the solution in liters, which contains a gram-molecular weight of the electrolyte. μ_v is the molecular conductivity at volume v.

TABLE I.

Molecular Conductivity of $2NaClZnCl_2$ (253.3).

v.	First series. $\mu_{v\ 25°}$.	Second series. $\mu_{v\ 25°}$.	Mean.
1.14	143.8	143.8	143.8
2.28	209.8	209.8	209.8
3.02	238.7	238.7	238.7
6.04	285.6	285.8	285.7
12.08	320.0	320.2	320.1
24.16	349.1	349.1	349.1
48.32	374.5	374.6	374.5
96.64	391.2	391.2	391.2
193.28	413.5	413.7	413.6
773.12	444.1	446.1	445.1
1546.24	468.3	468.4	468.3
3092.48	480.7	480.9	480.8
6184.96	486.7	488.5	487.6

In each determination of conductivity in the above and following tables, a number of resistances were used in the rheostat. Usually from two to four resistances were employed, the amount of the resistance being so chosen that the readings on the bridge were always between 400 mm. and 600 mm. Thus, each result given, is the average of from two to four conductivity measurements.

For the sake of comparing the conductivities of solutions of sodium zinc chloride, with the sum of the conductivities of the constituents at the same dilutions, we have taken the conductivity measurements of sodium chloride and zinc chloride as

determined by Kohlrausch, adding the proper temperature coefficients.

Since there are two molecules of sodium chloride in the double salt to one of zinc chloride, in making the comparison twice the molecular conductivity of sodium chloride at one-half the dilution must be taken.

TABLE II.

Comparison for $2NaCl.ZnCl_2$.

NaCl		$ZnCl_2$			$2NaCl.ZnCl_2$		Difference.
v.	μ_v 25°.	v.	μ_v 25°.	Sum.	v.	μ_v 25°.	
0.57	153.7	1.14	120.3	274.0	1.14	143.8	130.2
1.14	171.8	2.28	129.8	301.6	2.28	209.8	91.8
1.51	176.4	3.02	130.3	306.7	3.02	238.7	68.0
3.02	185.4	6.04	145.3	330.7	6.04	285.6	45.1
6.04	193.4	12.08	159.5	352.9	12.08	320.1	32.8
12.08	205.4	24.16	179.9	385.3	24.16	349.1	36.2
24.16	211.8	48.32	188.1	399.9	48.32	374.5	25.4
48.32	218.3	96.64	196.2	414.5	96.64	391.2	23.2
96.64	224.2	193.28	213.1	437.3	193.28	413.6	23.7
386.56	230.4	773.12	222.9	453.3	773.12	445.1	8.2
773.12	233.6	1546.24	228.7	462.3	1546.24	468.3	—6.0

The Double Chloride of Ammonium and Magnesium,

$NH_4Cl.MgCl_2.6H_2O$.

The double salt was prepared by bringing together in solution one equivalent of each constituent, and carefully evaporating the solution to crystallization. The salt must be allowed to crystallize slowly, but with proper precaution there is no serious difficulty in obtaining it in pure condition. The salt crystallized in columns. To test the purity of the compound used both water and magnesium were determined.

	Calculated.	Found.
H_2O	42.1	42.5
Mg	9.31	9.14

A solution of the double salt was prepared and carefully standardized by determining the magnesium in a known volume.

TABLE III.

Molecular Conductivity of $NH_4Cl.MgCl_2$ (148.75).

	First series.	Second series.	
v.	μ_v 25°.	μ_v 25°.	Mean.
1.92	201.8	201.8	201.8
3.84	229.6	229.2	229.4
7.68	252.9	252.9	252.9
15.36	274.8	274.8	274.8
30.72	295.5	295.9	295.7
61.44	312.6	313.2	312.9
122.88	327.4	327.4	327.4
245.76	340.9	340.9	340.9
491.52	349.8	349.8	349.8
983.04	358.5	360.4	359.5
1966.08	369.4	369.5	369.4
3932.16	381.4	380.4	380.9
7864.32	394.9	394.8	394.9

We determined the conductivities of solutions of both of the constituents of this double salt. The ammonium chloride used was the product of the third fractional crystallization of a good sample of the salt. The flame test showed no potassium, and a mere trace of sodium. The chloride was dried to constant weight in an air-bath at 140°, and a standard solution prepared from a weighed quantity of this substance. The magnesium chloride used was prepared by fractional crystallization of a fairly pure specimen of the salt. It was recrystallized twice, when the flame showed that all but a trace of impurities had been removed.

TABLE IV.

Molecular Conductivity of NH_4Cl (53.49).

	First series.	Second series.	
v.	μ_v 25°.	μ_v 25°.	Mean.
1	99.3	99.3	99.3
2	104.9	104.9	104.9
4	110.4	110.4	110.4
8	115.8	115.8	115.8
16	120.7	120.9	120.8
40	127.6	127.6	127.6
80	131.8	131.8	131.8
160	134.5	134.0	134.2
320	136.9	136.7	136.8
640	138.0	138.2	138.1
1600	138.9	139.0	138.9

The values which we found for the conductivity of ammonium chloride differed slightly from those obtained by Kohlrausch,[1] our values being somewhat lower in the more concentrated solutions, and a little higher in the more dilute. This difference is probably due to the temperature coefficient which must be added to Kohlrausch's values, to transform them from 18° to 25°. This coefficient is, at best, somewhat uncertain over any considerable range of temperature, and we are therefore inclined to use the values which we found directly at 25°, rather than Kohlrausch's values, to which an uncertain factor must be added.

We measured the conductivity of magnesium chloride directly at 25°, since the conductivity measurements hitherto made with this compound did not meet our requirements. Temperature coefficients are not given for all of the values obtained by Kohlrausch.[2] Vicentini[3] began his work at a dilution of 621 liters, and Walden,[4] who was the only one to work with this substance at 25°, began at a volume of 64 liters. We desired data at much greater concentrations.

TABLE V.

Molecular Conductivity of $MgCl_2$ (95.26).

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.76	126.3	126.3	126.3
3.52	143.3	143.3	143.3
7.04	159.8	159.8	159.8
14.08	175.4	174.8	175.1
35.20	190.3	190.3	190.3
70.40	201.1	201.1	201.1
140.8	211.3	211.4	211.3
281.6	221.1	221.1	221.1
563.2	227.4	227.5	227.4
1408.0	234.5	234.5	234.5
2816.0	242.8	243.6	243.2
5632.0	252.5	254.1	253.3
11264.0	260.4	261.6	261.0

Our values for magnesium chloride agree very well with those found by Walden, as far as the two series can be compared.

[1] Ann. Phys. (Wied.), **26**, 161. [2] *Loc. cit.*
[3] Atti. d. R. Accad. di Turino, **20**, 1885. [4] Ztschr. phys. Chem., **2**, 49.

TABLE VI.

Comparison for $NH_4Cl.MgCl_2$.

v.	NH_4Cl. μ_v 25°.	v.	$MgCl_2$. μ_v 25°.	Sum.	v.	$NH_4Cl.MgCl_2$. μ_v 25°.	Difference.
1.92	104.5	1.92	127.9	232.4	1.92	201.8	30.6
3.84	110.0	3.84	144.8	254.8	3.84	229.4	25.4
7.68	115.4	7.68	161.3	276.7	7.68	252.9	23.8
15.36	120.3	15.36	176.3	296.6	15.36	274.8	21.8
30.72	124.7	30.72	186.5	311.2	30.72	295.7	15.5
61.44	129.8	61.44	198.3	328.1	61.44	312.9	15.2
122.88	133.2	122.88	208.7	341.9	122.88	327.4	14.5
245.76	135.7	245.76	218.6	354.3	245.76	340.9	13.4
491.52	137.4	491.52	225.8	363.2	491.52	349.8	13.4
983.04	138.0	983.04	230.2	368.2	983.04	359.5	8.7
1966.08	138.0	1966.08	237.5	375.5	1966.08	369.4	6.1
3932.16	138.0	3932.16	246.6	384.6	3932.16	380.9	3.7
7864.32	138.0	7864.32	257.1	395.1	7864.32	394.9	0.2

The Double Chloride of Potassium and Magnesium,
$KCl.MgCl_2.6H_2O$.

One equivalent of potassium chloride was brought in solution with one equivalent of magnesium chloride, and the solution containing the mixture evaporated to crystallization. The double salt did not separate at first, but apparently considerable potassium chloride. After discarding a number of crops of crystals, there appeared well-defined crystals, which were evidently neither of the constituents. These were found, on analysis, to be the double chloride desired.

It is not a simple matter to obtain this salt in quantity. After the double salt began to crystallize the greatest care was necessary in concentrating the solution. To secure enough material for our work (about 100 grams) required nearly four months. Marignac[1] has already described the crystals.

The salt, as in all cases, was carefully dried by pressing between layers of filter-paper. The magnesium was determined with the following result:

	Calculated.	Found.
Mg	8.64	8.63

[1] Ann. des Mines, [5], 12, 3.

A solution of the double salt was standardized and the following conductivity measurements made. The conductivity of magnesium chloride had already been determined, and the values for potassium chloride are taken from the results of Kohlrausch.

TABLE VII.

Molecular Conductivity of $KCl.MgCl_2$ (169.85).

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.95	196.4	195.2	195.8
3.90	225.9	225.8	225.9
7.80	247.4	247.4	247.4
15.60	270.7	270.7	270.7
31.2	285.4	285.8	285.6
62.4	299.2	299.1	299.1
124.8	313.5	313.6	313.5
249.6	326.5	326.5	326.5
499.2	336.0	336.4	336.2
998.4	345.2	345.2	345.2
1996.8	357.5	358.7	358.1
3993.6	376.5	376.5	376.5
7987.2	394.6	394.7	394.6

The following comparison is made in all respects like the preceding for the double salt of magnesium and ammonium.

TABLE VIII.

Comparison for $KCl.MgCl_2$.

v.	KCl. μ_v 25°.	v.	$MgCl_2$. μ_v 25°.	Sum.	v.	KCl.$MgCl_2$. μ_v 25°.	Difference.
1.95	108.5	1.95	128.2	236.7	1.95	195.8	40.9
3.90	110.1	3.90	145.1	255.2	3.90	225.9	29.3
7.80	115.5	7.80	161.6	277.1	7.80	247.4	29.7
15.60	120.5	15.6	176.5	297.0	15.6	270.7	26.3
31.2	125.4	31.2	186.8	212.2	31.2	285.6	26.6
62.4	127.3	62.4	198.6	325.9	62.4	299.1	26.8
124.8	130.8	124.8	209.0	339.8	124.8	313.5	26.3
249.6	132.3	249.6	218.9	351.2	249.6	326.5	24.7
499.2	133.7	499.2	226.0	359.7	499.2	336.2	23.5
998.4	134.7	998.4	229.3	364.0	998.4	345.2	18.8
1996.8	135.7	1996.8	237.7	373.4	1996.8	358.1	15.3
3993.6	136.1	3993.6	246.8	382.9	3993.6	376.5	6.4
7987.2	136.7	7987.2	257.4	394.1	7987.2	394.6	—0.5

The Double Chloride of Strontium and Cadmium, $SrCl_2.2CdCl_2.7H_2O$.

One equivalent of strontium chloride and two equivalents of cadmium chloride were brought together in solution, and this was evaporated to crystallization. The double salt separated without any serious difficulty, and it was quite a simple matter to obtain the substance in quantity large enough for our work. Both the water and cadmium in the salt were determined.

	Calculated.	Found.
H_2O	19.35	19.36
Cd	34.50	34.20

Von Hauer[1] has already described the crystals.

A standard solution was prepared by determining the cadmium in a measured volume, and from this as a starting-point, the following conductivity measurements were made :

TABLE IX.

Molecular Conductivity of $SrCl_2.2CdCl_2$ (524.98).

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2.18	127.0	126.9	127.0
4.36	184.0	184.1	184.0
8.72	238.5	238.5	238.5
17.44	293.3	293.1	293.2
34.88	348.5	346.5	347.5
69.77	402.1	402.0	402.0
139.52	456.2	456.2	456.2
279.04	506.7	506.8	506.7
558.08	561.5	561.5	561.5
1116.16	613.8	613.7	613.7
2232.32	657.8	657.8	657.8
4464.64	701.5	701.4	701.5
8929.28	739.1	739.0	739.0
17858.56	774.8	774.0	774.4

The conductivity of each of the constituent chlorides was then determined. The measurements which have already been made with strontium chloride were not adequate to our purpose, and the conductivity of cadmium chloride as determined by Grotrian and Wershofen,[2] differed appreciably from the values found by Jones and Ota.[3]

[1] Sitzungs Bericht. Akad. d. Wissenschaft Wien., **15**, 23; **17**, 331.

[2] Ztschr. phys. Chem., **5**, 431; Ann. Phys. (Wied.), **18**, 177.

[3] This JOURNAL, **22**, 5.

TABLE X.

Molecular Conductivity of $SrCl_2$ (158.58).

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	108.5	108.5	108.5
2	130.1	130.0	130.0
4	146.6	146.6	146.6
8	162.6	162.6	162.6
16	179.4	179.6	179.5
40	196.2	196.0	196.1
80	207.4	207.3	207.4
160	219.0	219.0	219.0
320	229.6	229.0	229.3
640	237.6	237.6	237.6
1600	246.5	246.3	246.4
3200	252.5	252.4	252.5
6400	260.0	260.1	260.0
12800	270.2	270.0	270.1

Our values for the more concentrated solutions are lower than those of Kohlrausch,[1] while for the more dilute we found much greater conductivity than Vicentini.[2] Our values are, however, quite regular, the two series of measurements agreeing well with one another, and the differences between the conductivities as the dilution increases are as regular as could be expected. Furthermore, we were very careful to secure the salt in pure condition by fractional crystallization. The solution was standardized by determining the amount of strontium in a measured volume. The strontium was determined as carbonate. Two determinations of strontium in 5 cc. of the solution gave respectively:

First, 0.7406 gram of strontium carbonate.

Second, 0.7420 gram of strontium carbonate.

The two values are evidently quite concordant. We are unable to find any appreciable source of error in our work with this substance.

As the conductivity of cadmium chloride found by Grotrian and Wershofen differed from that found by Jones and Ota, we determined to repeat the measurements.

[1] *Loc. cit.* [2] *Loc. cit.*

TABLE XI.

Conductivity of $CdCl_2$ (183.2).

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.932	28.1	28.1	28.1
1.864	44.9	44.9	44.9
3.728	62.8	62.8	62.8
7.456	82.5	82.5	82.5
14.91	101.6	101.4	101.5
37.375	129.5	129.6	129.6
74.75	150.3	150.3	150.3
149.50	171.7	171.7	171.7
299.0	192.2	192.4	192.3
598.0	206.6	206.4	206.5
1495.0	227.7	227.6	227.6
2990.0	242.0	241.9	242.6
5980.0	255.3	255.3	255.3

Our values for cadmium chloride agree very satisfactorily with those obtained by Jones and Ota, and therefore differ quite appreciably from the results found by Grotrian and Wershofen.

TABLE XII.

Comparison for $SrCl_2.2CdCl_2$.

v.	$SrCl_2$. μ_v 25°.	v.	$CdCl_2$. μ_v 25°.	Sum.	v.	$SrCl_2.2CdCl_2$. μ_v 25°.	Difference.
2.18	131.5	1.09	61.9	193.4	2.18	127.0	66.4
4.36	148.1	2.18	94.3	242.4	4.36	184.0	58.4
8.72	164.4	4.36	132.2	296.6	8.72	238.5	58.9
17.44	180.5	8.72	171.6	352.1	17.44	293.2	58.1
34.88	192.6	17.44	209.4	402.0	34.88	347.5	54.5
69.76	204.6	34.88	252.5	457.1	69.76	402.0	55.1
139.5	216.8	69.76	295.1	511.9	139.5	456.0	55.9
279.0	224.5	139.5	337.5	562.0	279.0	506.7	55.3
558.1	235.6	279.0	379.0	614.6	558.1	561.5	53.1
1116.2	242.0	558.1	409.2	651.2	1116.1	613.7	37.5
2232.4	248.6	1116.2	436.1	684.7	2232.4	657.8	26.9
4464.8	258.3	2232.4	464.8	723.1	4464.8	701.5	21.6
8929.6	264.1	4464.8	496.7	760.8	8929.6	739.1	21.7

Discussion of the Results Obtained with Double Chlorides.

The problem, as already stated, is to determine whether these double chlorides exist to any extent as such in the solu-

tions, or break down completely into their constituents? If the latter is true, then the "difference" will either be zero if the solutions are isohydric," or it will have a small value if the solutions are not isohydric. If, on the contrary, the double salt exists to any appreciable extent in the solution, the value of the "difference" will be greater. In examining the results the point of direct interest is to examine the magnitude of what we have tabulated under the head of "difference." The first salt studied, *i. e.* the double chloride of sodium and zinc, shows unusually large differences in the concentrated solutions; indeed, larger differences throughout than was found by Jones and Mackay, and later by Jones and Ota[1] for the corresponding potassium zinc chloride. These differences diminish rapidly with increase in dilution, disappearing at a dilution of 500 to 600 liters. It seems strange that the sodium salt should show much larger differences than the potassium, but this is the case.

The values of the differences for the two double chlorides, potassium magnesium, and ammonium magnesium, are much less than for the salt just considered. Yet they are very appreciable. They are of about the same order of magnitude for the two salts, being somewhat greater throughout for the potassium than for the ammonium compound. These differences disappear in both cases in the more dilute solutions.

The differences for the double chloride of cadmium and strontium are much larger than for the magnesium salts, but much smaller than for the sodium zinc bromide. Furthermore, the differences in this case decrease much more slowly with increase in dilution than in any of the preceding salts. This shows that the double chloride of strontium and cadmium is capable of existing, to some extent, at greater dilution than any of the salts thus far studied.

Before any final conclusion can be drawn with reference to the condition of the double salts in solution, we must determine what effect the presence of one of the constituent chlorides has on the dissociation of the other chloride. It is well known that in solutions which are not isohydric, the presence

[1] *Loc. cit.*

of a substance with a common ion will drive back the dissociation of another substance. It might be possible that our differences are entirely or partially produced in this way, the conductivity of the double salt being less than the sum of the conductivities of the constituents, because each constituent drives back the dissociation of the other to some extent, and thus diminishes the conductivity of solutions of the double salt.

It is very important that the amount by which one chloride diminishes the conductivity of another should be determined by direct experiment. We could then see whether our "differences" are due to the action of one of the constituent chlorides on the conductivity of the other, or to the presence of a certain amount of the double salt in solution.

We have tried to settle this point experimentally, as follows: Two chlorides which could not form a double salt with one another were mixed in definite quantities, and the conductivity of the solution determined. Then the conductivity of each chloride was ascertained, separately, at the same dilution. The sum of the conductivities of the solutions of the single chlorides was then subtracted from the conductivity of the mixture at the same dilution. The resulting difference would necessarily be an expression of the sum of the effect of each chloride on the dissociation of the other.

Mixtures of Chlorides Which Do Not Form a Double Salt.

We chose potassium chloride and ammonium chloride as compounds which do not form double salts with one another. These were taken because they could be easily obtained in pure condition; indeed, we had already prepared pure specimens of both substances. We mixed a gram-molecular weight of potassium chloride with a gram-molecular weight of ammonium chloride, and dissolved the mixture to a liter of solution. This was used as the mother-solution for all the remaining dilutions. The conductivities of these solutions are given in the following table:

TABLE XIII.

Conductivities of Mixtures of $KCl + NH_4Cl$.

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	179.3	179.3	179.3
2	195.0	195.1	195.0
4	208.2	208.4	208.3
8	220.9	221.0	220.9
16	231.7	231.7	231.7
32	241.1	241.3	241.2
40	245.8	246.0	245.9
80	254.2	254.4	254.3
160	262.6	262.0	262.3
320	267.0	267.0	267.0
640	273.1	273.1	273.1
1600	279.2	279.0	279.1

TABLE XIV.

Comparison for $KCl.NH_4Cl$.

v.	KCl. μ_v 25°.	v.	NH_4Cl. μ_v 25°.	Sum.	v.	$KCl.NH_4Cl$. μ_v 25°.	Difference.
1	104.1	1	99.3	203.4	1	179.3	24.1
2	108.6	2	104.9	213.5	2	195.0	18.5
4	111.2	4	110.4	221.6	4	208.3	13.3
8	116.5	8	115.8	232.3	8	220.9	11.4
16	121.5	16	120.9	242.4	16	231.7	10.7
32	125.4	32	125.3	250.7	32	241.2	9.5
40	125.7	40	127.6	253.3	40	245.9	7.4
80	128.5	80	131.8	260.3	80	254.3	6.0
160	131.1	160	134.2	265.3	160	262.3	3.0
320	132.1	320	136.8	268.9	320	267.0	1.9
640	133.9	640	138.1	272.0	640	273.1	—1.1
1600	135.4	1600	138.9	274.3	1600	279.1	—4.8

A mixture was then prepared containing one equivalent of potassium chloride and two of ammonium chloride, and studied in exactly the same manner as the above mixture. This was done for the purpose of determining the effect when one of the constituents was in excess. The following results were obtained :

TABLE XV.

Conductivities of Mixtures of $KCl.2NH_4Cl$.

v.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	251.5	251.5	251.5
2	278.5	278.1	278.3
4	301.1	302.1	301.5
8	322.4	322.8	322.6
16	340.8	340.8	340.8
32	353.1	353.9	353.5
40	362.8	362.9	362.8
80	376.5	376.5	376.5
160	390.1	390.7	390.4
320	400.1	400.3	400.2
640	410.6	410.6	410.6
1600	414.1	415.7	414.9

TABLE XVI.

Comparison for $KCl.2NH_4Cl$.

v.	KCl. μ_v 25°.	v.	NH_4Cl. $2\mu_v$ 25°.	Sum.	v.	$KCl.2NH_4Cl$. μ_v 25°.	Difference.
1	104.1	0.5	188.6	292.7	1	251.5	41.2
2	108.6	1	198.6	307.2	2	278.3	28.9
4	111.2	2	209.8	321.0	4	301.5	19.5
8	116.5	4	220.8	337.3	8	322.6	14.7
16	121.5	8	231.6	353.1	16	340.8	12.3
32	125.4	16	241.8	367.2	32	353.5	13.7
40	125.7	20	244.0	369.7	40	362.8	6.9
80	128.5	40	255.2	383.7	80	376.5	7.2
160	131.1	80	263.6	394.7	160	390.4	4.3
320	132.1	160	268.4	400.5	320	400.2	0.3
640	133.9	320	273.6	407.5	640	410.6	—3.1
1600	135.4	640	277.8	413.2	1600	414.9	—1.7

If we compare the differenees with these mixtures which cannot form double salts, with the differences for the double salts, we are forced to the following conclusions: The mixture of 1 molecule of potassium chloride with 1 molecule of ammonium chloride, must be compared with the double salts containing 1 molecule of each chloride, in this case with potassium magnesium, and ammonium magnesium chlorides. The differences for the double salts are much larger than for the mixture, in the more concentrated solutions, and persist

to much greater dilutions. Thus, the difference entirely disappears in the mixture at about 500 liters, but does not disappear in the double salts until a dilution of several thousand liters is reached.

Comparing the differences for the mixture of 1 molecule of potassium chloride and 2 molecules of ammonium chloride, with those for the double chlorides containing 1 molecule of one chloride and 2 molecules of the other, the following relations appear. The differences for sodium zinc chloride are much greater than for the mixture, and persist at greater dilution. The differences for strontium cadmium chloride are not only much greater than for the mixture, at the same dilutions, but are very much more persistent, not disappearing at the greatest dilution with which we worked,—nearly 9,000 liters.

We seem then to be forced to the conclusion, that all four of these double chlorides exist, to a considerable extent, in the more concentrated solutions, and are broken down completely by water only at very high dilutions. This is the same conclusion as that reached by Jones and Ota[1] through their study of a number of double chlorides. But since they did not study mixtures of chlorides incapable of forming double salts, their conclusion was not based upon evidence as complete as that now at our disposal.

Freezing-point Lowering Produced by Double Chlorides.

Jones and Mackay[2] employed not only the conductivity method to throw light on the condition of double sulphates in solution, but also the freezing-point method. Jones and Ota[3] also attempted to apply the freezing-point method to the problem of double chlorides in solution, but as they were unable to obtain satisfactory results, they did not publish them.

Not content with the experience of Jones and Ota in this direction, we again attempted to apply the freezing-point method to the problem of the double chlorides. We first studied the freezing-point lowering of three of the double chlorides already investigated by the conductivity method. These were ammonium magnesium chloride, sodium zinc

[1] *Loc. cit.* [2] *Loc. cit.* [3] *Loc. cit.*

chloride, and strontium cadmium chloride. Below are given the volumes of the solutions used, and the molecular lowerings found at these volumes.

TABLE XVII.

Freezing-point Lowering of Double Chlorides.

$NH_4Cl.MgCl_2$.		$2NaCl.ZnCl_2$.		$SrCl_2.2CdCl_2$.	
Volume.	Molecular lowering.	Volume.	Molecular lowering.	Volume.	Molecular lowering.
1.92	9.48	3.03	12.27	2.18	9.31
3.84	8.71	6.06	11.84	4.36	9.83
7.68	8.52	12.12	11.71	8.72	10.51
15.36	8.63	24.24	11.84	17.44	11.18
30.72	8.89	48.48	12.47	34.88	11.90
61.44	9.31			69.76	12.67
122.88	9.65				

The molecular lowering of strontium cadmium chloride is regular, *i. e.*, increases throughout with increase in dilution. But the molecular lowerings of sodium zinc, and ammonium magnesium chlorides, are greater in the more concentrated solutions, decrease with increase in dilution to a minimum, and then increase from this point as the dilution increases. That there should be a minimum in the curve expressing the relation between concentration and molecular lowering is, of course, abnormal, and excluded the use of this method for the purpose of throwing light on the problem under investigation.

The freezing-point lowering of one of the constituents, magnesium chloride, was, however, determined. This had been found by Loomis[1] to give results of the same general character as those which we found for two of the double chlorides. The freezing-point curves showed a decided minimum. The results which we obtained for magnesium chloride are given in the following table:

TABLE XVIII.

Freezing-point Lowerings of $MgCl_2$.

Volume.	Molecular lowering.
1.76	5.70
3.52	5.14
7.04	4.88
14.08	4.98
28.16	5.30

[1] Ann. Phys. (Wied.), 57, 503.

Here again was clear evidence of a minimum in the freezing-point curve. We did not carry our work further in this direction. The problem of the freezing-point lowering of a number of single chlorides has since been taken up in this laboratory by Mr. V. J. Chambers. The results of his investigation will soon be published in this JOURNAL. It may be stated in advance that a minimum in the molecular lowering has been found for a number of chlorides and bromides, and we have a theory which we think will account for these apparently abnormal results.

Jones and Ota determined the freezing-point lowerings of the four double chlorides which they investigated. As their results have never been published they will now be given.

TABLE XIX.

Molecular lowering $2KCl.ZnCl_2$.		Molecular lowering $KCl.CdCl_2$.	
Volume.	Molecular lowering.	Volume.	Molecular lowering.
2	12.12	2	5.21
4	12.05	4	5.81
8	12.27	8	6.37
16	12.49	16	7.07
32	13.00	32	7.90
64	13.10	64	8.44
128	13.12	128	9.21

TABLE XX.

Molecular lowering $NaCl.AlCl_3$.				Mol. lowering $2NH_4Cl.HgCl_2$.	
Volume.	First series.	Volume.	Second series.	Volume.	Molecular lowering.
4.21	10.04	5.76	10.14	10	6.97
8.42	10.12	11.53	10.00	15	7.33
16.84	10.44	23.06	10.49	20	7.70
33.68	10.65	46.12	10.67	30	7.86
67.36	10.78	92.24	10.76		
134.72	11.04	184.48	10.86		

In neither of these four cases, with the possible exception of the first, is there any evidence of a minimum in the molecular lowering.

It is clear, from what has already been stated, that no light can be thrown on the nature of double chlorides in solution by the freezing-point method. We must be content with the evidence from the conductivity method alone.

DOUBLE BROMIDES.

The double bromides which we have studied are:

$$BaBr_2.CdBr_2.4H_2O,$$
$$KBr.CdBr_2.\tfrac{1}{2}H_2O,$$
$$2NaBr.3CdBr_2.6H_2O,$$
$$3NH_4Br.ZnBr_2.$$

These have been dealt with in exactly the same manner as the double chlorides. The conductivity of each constituent has been determined, then the conductivity of the double salt, and the sum of the former compared with the latter.

The Double Bromide of Barium and Cadmium,
$BaBr_2.CdBr_2.4H_2O$.

The constituent bromides were brought together in equivalent quantities, and then a slight excess of cadmium bromide added. The double salt crystallizes from this mixture in thick columns. The salt was analyzed both for water and cadmium with the following results:

	Calculated.	Found.
H_2O	11.22	11.52
Cd	17.5	17.2

TABLE XXI.

Molecular Conductivity of $BaBr_2.CdBr_2$ (569.55).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.97	126.0	126.1	126.0
3.94	166.0	166.0	166.0
7.88	205.9	205.5	205.7
15.76	243.7	243.8	243.7
31.52	276.6	276.7	276.6
63.04	309.7	309.7	309.7
78.08	324.0	324.8	324.4
156.16	357.7	357.7	357.7
312.32	392.4	392.4	392.4
624.64	428.0	429.0	428.5
1249.28	457.9	457.9	457.9
2498.56	481.9	481.7	481.8
3112.20	493.5	493.4	493.5
6226.40	518.9	519.0	518.9

We determined the conductivities of both constituent bromides, directly, at 25°. A solution of purified barium bromide was standardized and made the mother-solution for all the subsequent dilutions.

TABLE XXII.

Molecular Conductivity of $BaBr_2$ (297.34).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2	147.7	147.6	147.7
4	162.4	162.4	162.4
8	176.4	176.6	176.5
16	190.9	190.9	190.9
32	202.0	202.1	202.0
80	218.5	218.5	218.5
160	228.7	228.9	228.8
320	241.5	241.5	241.5
640	249.2	249.2	249.2
1280	257.1	257.2	257.1
3200	270.7	270.9	270.8
6400	280.8	280.8	280.8

A solution of purified cadmium bromide was standardized by determining the amount of cadmium oxide in a measured volume. From this all the remaining dilutions were made in the manner already described.

TABLE XXIII.

Molecular Conductivity of $CdBr_2$ (272.21).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2.60	41.3	41.3	41.3
5.20	57.4	57.4	57.4
10.40	75.7	75.7	75.7
20.80	95.0	95.2	95.1
41.60	115.3	115.4	115.3
104.0	144.1	144.3	144.2
208.0	166.1	166.0	166.0
416.0	188.9	188.7	188.8
832.0	209.3	209.3	209.3
1664.0	228.3	228.2	228.2
3328.0	242.5	242.3	242.4
6656.0	256.3	256.0	256.1

Since there is one molecule of barium bromide to one of cadmium bromide in the molecule of the double salt, the comparison is made by taking the sum of the constituents at the same dilution, and comparing this with the conductivity of the double salt at the same dilution.

TABLE XXIV.

Comparison for $BaBr_2.CdBr_2$.

v.	$BaBr_2$. μ_v 25°.	v.	$CdBr_2$. μ_v 25°.	Sum.	v.	$BaBr_2.CdBr_2$. μ_v 25°.	Difference.
1.97	147.5	1.97	37.3	184.8	1.97	126.0	58.8
3.94	162.0	3.94	49.7	211.7	3.94	166.0	45.7
7.88	176.1	7.88	66.6	242.7	7.88	205.7	37.0
15.76	190.1	15.76	85.4	275.5	15.76	243.7	31.8
31.52	201.7	31.52	105.2	306.9	31.52	276.6	30.3
63.04	212.0	63.04	125.0	337.0	63.04	309.7	27.3
78.08	218.2	78.08	132.3	350.5	78.08	324.4	26.1
156.16	228.1	156.16	155.3	383.4	156.16	357.7	25.7
312.32	240.8	312.32	177.4	418.2	312.32	392.4	25.8
624.64	248.9	624.64	199.0	447.9	624.64	428.5	19.4
1249.28	256.9	1249.28	218.8	475.7	1249.28	457.9	17.8
2498.56	264.2	2498.56	235.3	499.5	2498.56	481.8	17.7
3113.2	270.0	3113.2	241.0	511.0	3113.2	493.5	17.5
6226.4	280.1	6226.4	255.0	535.1	6226.4	518.9	16.2

The Double Bromide of Potassium and Cadmium,

$KBr.CdBr_2.\frac{1}{2}H_2O$.

To prepare the salt, one equivalent of potassium bromide was brought together with one equivalent of cadmium bromide. The salt was easily obtained in such quantity as we desired for our work. The cadmium in the salt was determined:

	Calculated.	Found.
Cd	28.04	27.76

We also determined the conductivity of solutions of potassium bromide using volumes ranging from 0.981 to 3140. The conductivity determinations hitherto made with this substance

by Kohlrausch,[1] Ostwald,[2] and Krannhals[3] did not cover the range of dilution desired.

TABLE XXV.

Molecular Conductivity of $KBr.CdBr_2$ (391.3).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.938	76.0	76.0	76.0
1.876	95.8	95.7	95.8
3.75	122.7	122.7	122.7
7.50	150.3	150.1	150.2
15.0	177.2	177.2	177.2
30.0	201.5	201.7	201.6
37.5	213.8	213.7	213.8
75.0	240.5	240.5	240.5
150.0	266.7	266.7	266.7
300.0	294.0	294.1	294.0
600.0	319.1	319.1	319.1
1200.0	342.1	342.4	342.2
1500.0	351.2	351.4	351.3
3000.0	370.7	370.7	370.7
6000.0	387.8	388.0	387.9

TABLE XXVI.

Molecular Conductivity of KBr (119.09).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.981	104.1	104.1	104.1
1.962	111.0	110.9	111.0
3.924	116.9	116.9	116.9
7.848	122.3	122.3	122.3
15.696	126.4	126.4	126.4
39.24	131.4	131.5	131.4
78.48	134.5	134.3	134.4
156.96	137.1	137.3	137.2
314.0	140.0	139.9	140.0
628.0	142.6	142.6	142.6
1256.0	145.1	145.1	145.1
1570.0	146.0	146.0	146.0
3140.0	146.7	146.7	146.7

[1] Ann. Phys. (Wied.), **6**, 1. [2] Ztschr. phys. Chem., **1**, 74.
[3] *Ibid.*, **3**, 250.

TABLE XXVII.

Comparison for KBr.CdBr₂.

v.	KBr. μ_v 25°.	*v.*	$CdBr_2$. μ_v 25°.	Sum.	*v.*	KBr. $CdBr_2$. μ_v 25°.	Difference.
0.938	103.5	....		....	0.938	76.0	...
1.876	110.8	....		....	1.876	95.8	...
3.750	116.4	3.75	48.4	164.8	3.75	122.7	42.1
7.50	121.8	7.50	65.5	187.3	7.50	150.2	37.1
15.0	126.0	15.0	84.3	210.3	15.0	177.2	33.1
30.0	129.4	30.0	104.1	233.5	30.0	201.6	31.9
37.5	131.0	37.5	111.3	242.3	37.5	213.8	28.5
75.0	134.2	75.0	130.7	264.9	75.0	240.5	24.4
150.0	136.9	150.0	153.9	290.8	150.0	266.7	24.1
300.0	139.7	300.0	176.1	315.8	300.0	294.0	21.8
600.0	142.4	600.0	197.9	340.3	600.0	319.1	21.2
1200.0	144.9	1200.0	217.8	362.7	1200.0	342.2	20.5
1500.0	146.8	1500.0	224.6	371.4	1500.0	351.3	20.1
3000.0	146.7	3000.0	242.4	389.1	3000.0	370.7	18.4
6000.0	147.0	6000.0	256.0	403.0	6000.0	387.9	15.1

A New Double Bromide of Sodium and Cadmium,

$2NaBr.3CdBr_2.6H_2O$.

We brought the constituent bromides together in the proportion to form the double salt, $2NaBr.2CdBr_2.5H_2O$, which is described in the literature. A beautifully crystallized salt separated in plates, and was supposed to be the one described. The cadmium in the double salt was determined.

	Found. I.	II.
Cd	30.0	29.6

The water was determined by drying a weighed portion of the salt to constant weight at 160°.

	Found. I.	II.
H_2O	10.5	10.3

The bromine was then determined.

	Found. I.	II.
Br	56.47	56.63

The cadmium, water, and bromine, correspond to a salt having the composition expressed by the formula:

$2NaBr.3CdBr_2.6H_2O$.

	Calculated.
Cd	29.8
H_2O	9.55
Br	56.59

A solution of the double salt was prepared and standardized, by determining the amount of cadmium in a known volume of the solution. From this standardized solution all the remaining dilutions were prepared. The conductivity of sodium bromide was determined over the range of dilutions desired. That of cadmium bromide had already been determined.

TABLE XXVIII.

Molecular Conductivity of $2NaBr.3CdBr_2$ (1022.63).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
2.443	132.8	132.4	132.6
4.886	187.4	187.6	187.5
9.772	248.0	248.2	248.1
19.544	315.9	316.0	315.9
39.088	387.0	387.0	387.0
78.176	457.7	457.8	457.7
97.72	478.3	478.3	478.3
195.44	548.3	548.3	548.3
390.88	625.1	625.5	625.3
781.76	701.6	701.6	701.6
1563.52	780.0	781.6	780.8
3908.80	856.0	857.5	856.8
7817.6	910.7	910.7	910.7
15635.2	958.5	962.4	960.4

TABLE XXIX.

Molecular Conductivity of NaBr (103.0).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1	80.6	80.0	80.3
2	88.0	88.0	88.0
4	94.4	94.4	94.4
8	100.6	101.0	100.8
16	105.3	105.3	105.3
40	110.6	111.1	110.8
80	113.1	113.1	113.1
160	116.6	116.6	116.6
320	119.0	119.4	119.2
640	120.9	120.9	120.9
1600	121.1	121.2	121.1

In comparing the conductivity of the double salt with the sum of the conductivities of the constituents, twice the molecular conductivity of sodium bromide at one-half the dilution of the double salt is taken. To this is added three times the molecular conductivity of cadmium bromide at one-third the dilution of the double salt. The reason for this is apparent from the composition of the double salt.

TABLE XXX.

Comparison for 2NaBr.3CdBr$_2$.

Volume.	NaBr. $2\mu_v$ 25°.	Volume.	$CdBr_2$. $3\mu_v$ 25°.	Sum.	Volume.	$2NaBr.3CdBr_2$. μ_v 25°.	Difference.
2.443	179.5	1.63	90.9	270.4	4.88	187.5	82.9
4.886	189.6	3.26	135.9	325.5	9.77	248.1	77.4
9.772	203.6	6.51	185.7	389.3	19.54	315.9	73.4
19.544	212.0	13.03	241.1	453.1	39.09	387.0	66.1
39.088	220.8	26.06	300.0	520.8	78.18	457.7	63.1
48.86	222.6	32.6	318.1	540.7	97.72	478.3	62.4
97.72	227.8	65.1	383.1	610.9	195.44	548.3	62.6
195.44	234.6	130.3	448.1	682.7	390.88	625.3	57.4
390.88	239.6	260.6	515.4	755.0	781.76	701.6	53.4
781.76	242.0	521.2	591.7	833.7	1563.52	780.8	52.9
1563.53	242.4	1302.9	657.9	900.3	3908.8	856.8	43.5
3908.8	242.5	2605.9	705.0	947.5	7817.6	910.7	37.8
7817.6	242.5	5211.7	750.9	993.4	15635.2	960.4	33.0

A New Double Bromide of Ammonium and Zinc,

$3NH_4Br.ZnBr_2$.

The constituent bromides were brought together in the proportion to form the double bromide, $2NH_4Br.ZnBr_2$, as described. After about two months 100 grams of a well-crystallized salt were obtained, and this was analyzed. One analysis showed the salt to contain 12.8 per cent of zinc, and a second analysis gave 12.6 per cent. The percentage of zinc in the salt $2NH_4Br.ZnBr_2.H_2O$, is 14.9. We concluded that either there was present a second double salt containing more than 2 molecules of ammonium bromide to 1 of zinc bromide, or that some ammonium bromide had crystallized out along with the double salt. A careful examination of the crystals showed that some were apparently of different habit from the remainder, being relatively much longer. It therefore seemed probable that we were dealing with a mixture.

The attempt was then made to recrystallize the salt. We were, however, unable to obtain it a second time, until a large quantity of a solution of the mixture $2NH_4Br.ZnBr_2$ was added. The salt crystallized readily out of this mixture, but again in both the longer and shorter crystals. The longer crystals were now separated mechanically from the shorter, and analyzed.

	Calculated for $3NH_4Br.ZnBr_2$.	Found. Longer crystals.	Shorter crystals.
Zn	12.6	12.8	12.5

To determine whether the salt contained water of crystallization, 3.4428 grams were heated for four hours in an air-bath, at 130°. The loss was 0.9 per cent. The salt was then further heated for four hours at 160°, when a slight decomposition took place. The total loss in weight amounted to only 1 per cent. It was therefore concluded that the salt contained no water of crystallization, the slight loss in weight observed being due to water which could not be removed by drying-paper, on account of the hygroscopic nature of the salt.

The bromine in the salt was then determined by two analyses, and found to be 77.24 per cent. The bromine calculated for $3NH_4Br.ZnBr_2$ is 77.01 per cent.

A standard solution of the salt was prepared by determining the zinc in a measured volume of the mother-solution.

TABLE XXXI.

Conductivity of $3NH_4Br.ZnBr_2$ (519.37).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
1.623	280.1	280.5	280.3
3.246	367.2	367.2	367.2
6.492	417.0	418.1	417.5
12.984	458.9	459.0	458.9
25.968	496.1	496.2	496.1
51.93	518.6	518.6	518.6
64.92	524.9	524.9	524.9
129.84	552.0	553.0	552.5
259.68	570.8	570.9	570.8
519.36	596.4	596.8	596.6
1038.72	621.7	621.8	621.7
2077.4	641.9	641.9	641.9
2596.8	651.0	651.1	651.0
5193.6	675.9	675.9	675.9

The molecular conductivity of ammonium bromide was determined, with a specimen which had been repeatedly crystallized, starting with a large quantity of fairly pure salt.

TABLE XXXII.

Molecular Conductivity of NH_4Br (98.02).

Volume.	First series. μ_v 25°.	Second series. μ_v 25°.	Mean.
0.92	100.0	100.0	100.0
1.84	106.0	106.1	106.0
3.68	111.4	111.2	111.3
7.36	117.3	117.3	117.3
14.72	121.8	122.0	121.9
36.8	127.9	127.7	127.8
73.6	130.9	131.0	130.9
147.2	133.9	133.9	133.9
294.5	137.0	137.3	137.1
588.8	139.7	139.6	139.6
1472.0	141.3	141.1	141.2

The conductivity of zinc bromide in water could not be determined directly, since the bromide is so readily decomposed by water. By comparing a number of chlorides and bromides we find the conductivity of the latter to be about 2 units greater than the former, for equal concentrations. To obtain the conductivity of zinc bromide at any dilution, we have taken the conductivity of zinc chloride at that dilution and added 2 units. This is, of course, only approximate, but is the best that can be done under the conditions. This could not be done, even approximately, for cadmium bromide, since it is well known that the cadmium halides show abnormally small dissociation, and this decreases very rapidly from the chloride to the iodide. While this same phenomenon begins to manifest itself with zinc, yet it is very much less pronounced than with cadmium. The error in the conductivity of zinc bromide, as calculated above, cannot be very great.

TABLE XXXIII.

Comparison for $3NH_4Br.ZnBr_2$.

v.	NH_4Br. $3\mu_v$ 25°.	v.	$ZnBr_2$. μ_v 25°.	Sum.	v.	$3NH_4Br.ZnBr_2$. μ_v 25°.	Difference.
0.541	285.0	1.623	80.0	365.0	1.623	280.3	84.7
1.082	303.0	3.246	132.5	435.5	3.246	367.2	68.3
2.164	321.3	6.492	148.4	469.7	6.492	417.5	52.2
4.328	337.2	12.984	164.2	501.4	12.984	458.9	42.5
8.656	354.3	25.968	183.9	538.2	25.968	496.1	42.1
21.64	371.4	64.92	192.7	564.1	64.92	524.9	39.2
43.28	385.5	129.84	206.6	592.1	129.84	552.5	39.6
86.56	393.9	259.68	216.6	610.5	259.68	570.8	39.7
173.13	399.0	519.36	222.6	621.6	519.36	596.6	25.0
346.24	411.0	1038.72	226.1	637.1	1038.72	621.7	15.4
865.6	420.0	2596.8	234.5	654.5	2596.8	651.0	3.5
1731.1	423.9	5193.6	237.0	670.9	5193.6	675.9	−5.0

Discussion of the Results Obtained with Double Bromides.

Examining the results obtained with the double bromides as with the double chlorides, the chief point of interest is the magnitude of the "differences" found. These are quite large in the concentrated solutions of barium cadmium bromide, and diminish slowly with increase in dilution. They do not disappear even at a dilution of 6,000 liters. This is strictly analogous to what was observed in the case of the double chloride of strontium and cadmium, the differences persisting in greater dilutions of this chloride than in either of the other double chlorides studied.

The differences for potassium cadmium bromide are almost exactly of the same magnitude as for the barium cadmium bromide, and persist, with increase in dilution, to almost exactly the same extent. The differences for the double bromide of sodium and cadmium are very great in the more concentrated solutions, and diminish comparatively slowly with increase in dilution. Indeed, at a dilution of 7,000 liters the difference is still 33 conductivity units. The differences for the double bromide of ammonium and zinc are large in the more concentrated solutions, but not as large, for equal dilution, as for the double bromide of sodium and cadmium. Furthermore, these differences decrease much more rapidly with increase in

dilution, entirely disappearing at about 1,000 liters. We did not study the effect upon one another of mixtures of bromides incapable of forming double salts, partly from lack of time, and partly because it is almost certain that the same general result would be obtained as with the chlorides.

From the above results with double bromides we think we are justified in drawing the same conclusion as in the case of the double chlorides; *viz.*, that *all four of the double bromides studied exist, to a considerable extent, in the more concentrated solutions, and are completely broken down by water only at very great dilutions.*

Ostwald[1] has made a sharp distinction between "double salts" and "complex salts." "The name double salt is not to be applied to any compound of two salts, which shows other reactions than its constituents. In all of these cases the constituents have undoubtedly united to form a more complex compound, which yields new ions, and must be regarded as a unit." Potassium platinum chloride is cited as a typical complex compound, since it breaks down with water into 2Na and $PtCl_6$. The double compounds, according to Ostwald, can be easily distinguished, since the lowering of the freezing-point and rise in boiling-point produced by them, are simply the sum of those produced by the constituents. Similarly, the electrical conductivity is the sum of the conductivities of the constituents.

In terms of this distinction, the double chlorides and bromides, which we have studied, cannot be classed as true double salts, since their conductivity is not the sum of the conductivities of their constituents. This obtains for all, in the more concentrated solutions, but, what is of far greater importance in this connection, it obtains, for several of the salts investigated in very dilute solutions. This is true especially of strontium cadmium chloride, of barium cadmium bromide, and of ammonium zinc bromide.

Before we can determine whether these salts are true complex salts, their solutions must be electrolyzed. If they are salts of true complex acids, when they are electrolyzed the more alkaline metal will go to the cathode, and the more acid

[1] Ztschr. phys. Chem., 3, 599.

metal to the anode. Thus, strontium cadmium chloride would break down in water into a strontium cation, and the cadmium would combine with the chlorine, forming the anion, just as the salt, K_2PtCl_6 breaks down into the ions K_2 and $PtCl_6$.

This problem we propose to investigate. We shall subject both the more concentrated and the more dilute solutions of double halides to the action of the current, and thus learn the nature of the ions formed.

We also propose to investigate a number of other classes of double or complex compounds, to see how they are broken down by water. We also hope to be able to subject some of these to the action of solvents other than water, to see how they are broken down by the different solvents.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1899.

Contributions from the Sheffield Laboratory of Yale University.

LXXI.—ON THE REARRANGEMENT OF THE THIONCARBAMIC ESTERS.

BY H. L. WHEELER AND BAYARD BARNES.

In the year 1849 Debus[1] found that when xanthogenamide, sulphourethane, sulphocarbamic ethyl ester or ethyl thioncarbamate[2] is heated, it is decomposed into ethyl mercaptan and cyanuric acid. This is, perhaps, not what would be expected of a compound having the structure $H_2NCS.OC_2H_5$. Its structure is shown, however, by its method of preparation from the xanthogenic esters and ammonia:

$$C_2H_5OCS.SC_2H_5 + NH_3 = C_2H_5OCS.NH_2 + HSC_2H_5.$$

With alkali it is decomposed normally, according to Debus,[3] into alcohol and sulphocyanate. C. Liebermann,[4] commenting on this behavior in 1881, states: "Es ist nicht unmöglich, dass man diese Reaction durch eine Umlagerung vielleicht in das von Salomon[5] entdeckte carbonylsulfäthylamin

[1] Ann. Chem. (Liebig), **72**, 18.

[2] In naming these substances the writer has employed the Geneva nomenclature *thion* and *thiol*. By this means the position of the sulphur can best be indicated, *thion* being used for compounds containing the group —CS.OR, and *thiol* for those containing the group —CO.SR.

[3] Ann. Chem. (Liebig), **73**, 149. [4] *Ibid.*, **207**, 165.

[5] J. prakt. Chem. [2], **7**, 256.

[ethyl thiolcarbamate $H_2NCO.SC_2H_5$] erklären muss, wofür auch der Umstand spricht, das die einmal begonnene Reaction von selbst fortschreitet."

Liebermann, however, did not test this explanation or assumption.

It seemed to the writer that if the thioncarbamic esters are capable of rearrangement into the isomeric thiol derivatives this reaction would be aided by alkyl iodides. The iodides would unite with the esters forming, at least, an intermediate addition-product—somewhat analogous to the sulphonium compounds—which would then give up alkyl iodide in another manner.

This seemed probable, as Jeanjean[1] found that dithiocarbamic ethyl ester gives a crystalline compound with ethyl iodide, $H_2NCS.SC_2H_5 + C_2H_5I$, while the work of Claus,[2] Bernthsen,[3] Wallach,[4] and others has shown that the thioamides in general form similar addition-products with alkyl halides.

We therefore heated 10 grams of ethyl thioncarbamate with 5 grams of ethyl iodide for a number of hours in a sealed tube, at 92°–96°. On cooling and opening the tube ethyl mercaptan and a compound having the properties of cyanuric acid were obtained. Under these conditions the reaction had proceeded as Debus found when the amide was submitted to distillation. Evidently this treatment was too energetic.

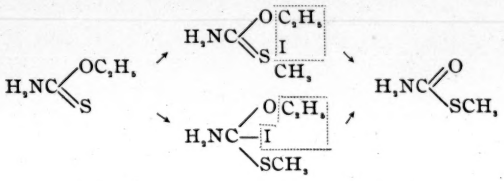
We then tried the action of ethyl iodide at ordinary temperature, when it was found that the rearrangement took place readily.

With methyl iodide the rearrangement is most striking. When methyl thioncarbamate (methyl xanthogenamide), melting at 43°, is mixed with a molecular proportion of methyl iodide, it dissolves, the temperature of the solution sinks, and then in a few minutes becomes warm enough to boil off the methyl iodide, and the whole solidifies to a shining mass of flattened prisms or plates. The material, after this treatment, melts at 105°–107°, and is, in fact, methyl thiolcarbammate, the carbonylsulfmethylamine of Blankenhorn.[5] The

[1] Jahresb., (1866), 501. [2] Ber. d. chem. Ges., 8, 41.
[3] Ann. Chem. (Liebig), 192, 56. [4] Ber. d. chem. Ges., 11, 1594.
[5] J. prakt. Chem., 16, 379.

methyl group has been transferred from the oxygen to the sulphur, and the thion compound has been transformed into a thiol :

This interesting rearrangement is undoubtedly the result of a series of reactions, the alkyl iodide separating into its constituents, alkyl and iodine, the constituents being added to the sulphur, and then separating alkyl from the oxygen along with iodine from the sulphur. This, perhaps, is best shown by the behavior of ethyl thioncarbamate (ethyl xanthogen amide) with methyl iodide, the action taking place with the same ease as with the methyl compound. This may be represented in either of the following two ways :



That is, either the alkyl iodide forms a tetravalent sulphur addition-product or it is added to the double union between sulphur and carbon. At any rate, from ethyl thioncarbamate and methyl iodide, methyl thiolcarbamate and ethyl iodide are obtained.

We have prepared a series of thioncarbamic esters and find that they all undergo this change easily with alkyl iodides. This rearrangement, moreover, is not confined to the action of iodides. Ethyl bromide, and even ethyl chloride, converts ethyl thioncarbamate into ethyl thiolcarbamate.

It might be expected now that ethyl thioncarbamate with ethylene bromide would give the compound

$$H_2NCO.SCH_2.CH_2.Br.$$

This, however, is not the case. As commonly observed with

ethylene bromide, both halogens react at once, and the ethylene ester of thiolcarbamic acid results,

$$H_2NCOSCH_2CH_2SCONH_2,$$

along with ethyl thiolcarbamate, the latter resulting from the action of ethyl bromide which is evolved in the reaction.

George Pinkus,[1] in his work on the action of trimethylene chlorobromide on thioamides, obtained in the case of xanthogenamide, a product to which he assigns the empirical formula

$$C_4H_8NOS\frac{Br + Cl}{2}.$$

He states that in the reaction ethyl bromide was evolved and the product melting from 102°–103° gave with potassium hydrate an offensive odor. It is now evident that in this experiment Pinkus had effected a rearrangement of the xanthogenamide without recognizing it, and that his product corresponds to a mixture of equal parts ω-chlor- and ω-brompropyl thiolcarbamates.

We have found that ethyl thioncarbamate reacts readily with chloracetic acid and other halogen compounds. These reactions will be described in a later paper. At present we have not examined the substituted thioncarbamic esters RNHCSOR′ and RNR″CSOR′, but we intend to do this later.

The above rearrangements, taking place as they do at ordinary temperatures, alter our views in regard to the structure of certain salts of thio- or sulphocarbamic acids. Neither thioncarbamic acid, $H_2NCS.OH$, or thiolcarbamic acid, H_2NCOSH, is known, and according to Beilstein[2] only salts of thiolcarbamic acid have been obtained.

The formation of the ammonium salt, when carbon oxysulphide and ammonia combine,[3] is represented as follows:

$$COS + 2NH_3 = H_2NCO.SNH_4.$$

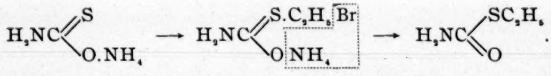
This thiol structure was established by the work of Fleischer,[4] who found that the salt gives with ethyl bromide at 100°, ethyl thiolcarbamate. Fleischer therefore concluded that this result settled his controversy with Claus,[5] who con-

[1] Ber. d. chem. Ges., **26**, 1077. [2] Handbuch d. org. Chem. [3], **1**, 1258.
[3] Berthelot: Jahresb., (1868), 160. [4] Ber. d. chem. Ges., **9**, 991.
[5] *Ibid.*, **9**, 723.

sidered the compound a thion derivative. Previously, Kretzschmar[1] assigned the thiol structure to this salt, chiefly because it gives urea and hydrogen sulphide when heated. Schmidt[2] came to the same conclusion.

Since now the action of ethyl bromide cannot be used to distinguish between a thiol or thion structure in this class of substances, it seems to the writer that the view of Claus is the best; *i. e.* the ease with which this salt is desulphurized points to the formula $H_2NCSONH_4$. This view is confirmed by the fact that $H_2NCS.OC_2H_5$ is readily desulphurized by silver nitrate while $H_2NCOSC_2H_5$ gives a stable silver salt.

The action of ethyl bromide on this salt is therefore to be represented in precisely the same manner as shown above in the case of the thioncarbamic esters :



The questions now arise : Is this reaction a general one for thion compounds ? Will compounds of the structure ROCS.OR give ROCO.SR, and ROCS.SR be transformed into RSCO.SR? Do the salts of the thioncarbonic acids react tautomerically with alkyl halides ?

With the exception of the above series and the alkyl sulphur derivatives of carbonic acid little is known of the thion compounds containing the grouping —CS.OC_2H_5. One salt of thionethylcarbonic acid has been described. Klason[3] states that carbon sulphochloride, $CSCl_2$, and sodium ethylate give $C_2H_5OCSONa$. With this exception it is noteworthy that all the salts of thio- and dithiocarbonic acids hitherto described have the thiol structure assigned to them.

This work also suggests that under suitable conditions a rearrangement may perhaps be expected in the case of tetravalent sulphur compounds; for example, a shifting of alkyl from oxygen to sulphur may be expected in the case of the esters of the sulphinic acids thus giving sulphones :

[1] J. prakt. Chem., **7**, 475. [2] Ber. d. chem. Ges., **10**, 191.
[3] *Ibid.*, **20**, 2384.

The alkyl sulphites may be transformed into alkyl sulphonic esters, etc.,

$$C_2H_5O—SO—OC_2H_5 \longrightarrow C_2H_5SO_2OC_2H_5.$$

Preliminary experiments by Mr. T. B. Johnson with benzenesulphinic ethyl ester and by Mr. R. J. Donnelly with ethyl dithiocarbonate, $C_2H_5OCSSC_2H_5$, show that these compounds are not transformed under the same conditions as the thioncarbamic esters, there being little, if any, tendency of the former, less positive, molecules to undergo change with ethyl iodide.[1]

In the case of the alkali and ammonia salts of thioncarbonic acid the molecule is even more positive than in the case of the thioncarbonic esters; therefore it appears that these compounds should react tautomerically.

We wish to reserve for this laboratory the examination of these questions and the study of the rearrangement of thion derivatives with organic halogen compounds in general, and work along these lines is now in progress here.

EXPERIMENTAL PART.

The thioncarbamic esters were prepared in the usual manner by the action of ammonia on the dithiocarbonic esters, and the latter were prepared by means of ethyl bromide from the potassium xanthogenates.

Methyl Thiolcarbamate from Methyl Thioncarbamate.—One gram of the latter was mixed with 1.5 grams of methyl iodide. On dissolving the solution became cool, then warm, and the product separated in a solid mass of crystals melting at 105°–107°. On crystallizing from water it melted at 107°–108°.

[1] It seems that basicity plays an important part in these addition reactions. It is probably due to the basicity of the molecules that the salts of the sulphinic acids give sulphones, and that the salts of sulphurous acid give the unsymmetrical derivatives with alkyl halides. Owing to the acid character of the molecules it appears improbable that the nitrites will be changed to the nitroparaffins by alkyl iodides. In the case of the more positive salts of nitrous acid, which act tautomerically, the behavior is precisely what would be expected of an addition-reaction. The higher alkyl iodides, which in general have less tendency to take part in addition-reactions, owing perhaps to stereochemical interference, give chiefly nitrites with these salts, while in the case of the lower halides the nitroparaffins result. In this connection the inertness of β-ethoxycrotonic ethyl ester may be mentioned. This compound can be heated with ethyl iodide for hours at 170°–180° without being converted into ethyl acetoacetic ester, and it can be boiled with benzoyl chloride and recovered unaltered.

Blankenhorn[1] obtained this compound from potassium sulphocyanide, methyl alcohol, and hydrochloric acid, but probably not in a pure condition, since he states that the melting-point lies between 95° and 98°. In all other respects our compound agrees with Blankenhorn's description. In 20 per cent alcoholic solution it gave a yellowish-white, curdy precipitate with silver nitrate. Platinum chloride gave an orange-yellow, mercuric chloride a white, and cupric sulphate a dirty white precipitate. These precipitates did not alter on standing.

Methyl thiolcarbamate is easily soluble in ether and in alcohol, but less readily in water, from which it separates in large, shining, colorless plates that have a talc-like consistency. It is somewhat volatile with steam. Warmed with aniline it evolves methyl mercaptan and ammonia and diphenylurea remains. This carbamate is identical in every respect with the following:

Methyl Thiolcarbamate from Ethyl Thioncarbamate.—The ethyl thioncarbamate used in this and other experiments melted at from 40°–41° and not at 38°, as stated by Salomon.[2] It was purified by dissolving it in ether and precipitating with petroleum ether, when it was obtained in beautiful, square, thick tables.

When 5.5 grams of this material were dissolved in 10 grams of methyl iodide the solution became cold, but on standing a few minutes heat was evolved, and a mass of plates separated. On crystallizing these from water they melted at 107°–108°. A nitrogen determination gave the following result:

	Calculated for $H_2NCO.SCH_3$.	Calculated for $H_2NCOSC_2H_5$.	Found.
N	15.38	13.33	15.84

It was found that the melting-points of methyl and ethyl thiolcarbamates are identical; they melted side by side at the same temperature in the same apparatus. In order, therefore, to confirm our analytical result and prove that methyl and not ethyl thiolcarbamate results in this reaction, Mr. W. M. Saunders performed the following experiment to determine whether our product with aniline gives methyl mercaptan (a

[1] J. prakt. Chem. [2], **16**, 375. [2] *Ibid.* [2], **8**, 115.

gas) or ethyl mercaptan (a liquid boiling at 36°), and also to identify the products of the reaction: Two grams of the product obtained by acting on ethyl thioncarbamate with methyl iodide were heated with about 2 molecules of aniline to 160° in an oil-bath, when over 350 cc. of gas was obtained which was collected over water. Ammonia and the odor of mercaptan were noticed. The gas passed into a solution of mercuric cyanide gave a finely divided white precipitate, which, purified by means of alcohol, in which it is very difficultly soluble, melted with decomposition at 170°–175°. The residue left on heating was crystallized from alcohol when diphenylurea was obtained melting at 234°–236°. There is, therefore, no doubt that methyl thiol carbamate is formed in the above reaction, and the action with aniline proceeds as follows:

$$\begin{matrix} NH_2 \\ CO \\ SCH_3 \end{matrix} \begin{matrix} H \\ \\ H \end{matrix} \begin{matrix} HNC_6H_5 \\ \\ HNC_6H_5 \end{matrix} = \begin{matrix} NHC_6H_5 \\ CO \\ NHC_6H_5 \end{matrix} + CH_3SH + NH_3.$$

Ethyl Thiolcarbamate from Ethyl Thioncarbamate.—When a portion of ethyl thioncarbamate (xanthogenamide) was dissolved in ethyl iodide, and the solution allowed to stand, a mass of silver-white plates remained after spontaneous evaporation of the iodide. These melted at 107°–108°. Another portion was allowed to stand only an hour when the material melted below 60°, the rearrangement then, not being complete, the solution was warmed on the water-bath, when it soon solidified. This rearrangement, therefore, takes place with greater difficulty than in the case of the methyl carbamate. The material in this instance, melting at 107°–108° and needing no purification, was simply pressed on paper and dried in the air. A nitrogen determination gave the following:

	Calculated for $H_3NCO.SC_2H_5$.	Found.
N	13.33	13.02

This product gave the reactions for "carboxylsulfäthylamin" as described by Konrad and Salomon.[1] Although, as stated, the melting-point of this compound is identical with

[1] J. prakt. Chem., 10, 35.

that of the methyl derivative, a mixture of the two was found to melt below 89°.

In another experiment ethyl thioncarbamate (5 grams) and ethyl bromide (6 grams) were heated for an hour on the water-bath, when it was found that a rearrangement had taken place, the product being identical with the above.

Isopropyl Thiolcarbamate from Isoamyl Thioncarbamate.—Ten grams of the latter were heated with 12 grams of isopropyl iodide on the steam-bath for two days. On cooling, a mass of crystals was obtained. These were washed with warm petroleum ether and crystallized twice from water when the material was obtained in colorless rectangular plates melting at about 125°. A nitrogen determination gave :

	Calculated for $H_2NCOSC_3H_7$.	Found.
N	11.76	11.84

The behavior of this material with silver nitrate, mercuric chloride, copper sulphate, and platinum chloride is identical with that of isobutyl thiolcarbamate and the other members of this series.

Isobutylthion carbamate was obtained by Mylius[1] from "isobutyldioxysulfocarbonat" and alcoholic ammonia. He states that it forms yellowish-white tables (from alcohol) melting at 36°. Blankenhorn[2] obtained this mixed with the thiol compound by treating potassium sulphocyanide in isobutyl alcohol with hydrochloric acid. He describes his product as a yellow oil crystallizing at 6° and melting at 10°. Our compound prepared from $C_4H_{11}O.CS.SC_2H_5$ and alcoholic ammonia readily solidified, and on crystallizing once from ether and then from water, melted at 51°–53°. It forms a snow-white mass of plates, and a nitrogen determination gave the following :

	Calculated for $H_2NCS.OC_4H_9$.	Found.
N	10.52	10.40

Isobutyl thioncarbamate in dilute alcoholic solution gives with silver nitrate a white precipitate which soon turns black (difference from thiolisobutylcarbamate). Mercuric chloride

[1] Ber. d. chem. Ges., **5**, 976. [2] J. prakt. Chem. [2], **16**, 380.

gives a white precipitate which can be boiled with water without change of color. Copper sulphate gives a white precipitate which, when warmed, changes to black. Platinum chloride gives a yellow precipitate which, when warmed, decomposes.

Isobutyl Thiolcarbamate from Isobutyl Thioncarbamate.—Five grams of the above material, melting at 51°–53°, were heated with 1 gram of isobutyl iodide, on the water-bath, for two hours, and on taking out a portion it was found to melt unaltered at 51°–53°. It was then heated in an oil-bath to 120° for several hours. On cooling, and crystallizing the material from water, it was then found to melt at 102°–103°. It thus separates in magnificent snow-white plates of extreme thinness. A nitrogen determination gave:

	Calculated for $H_2NCOSC_4H_9$.	Found.
N	10.52	10.45

Isobutyl thiolcarbamate closely resembles the other members of the thiol series. It is readily soluble in the ordinary solvents, except cold water, and it is volatilized with steam. Silver nitrate added to its dilute alcoholic solution produces a white precipitate which does not alter on standing. With mercuric chloride it behaves like the thion compound. With copper sulphate no precipitate is obtained in the cold, but on warming a white precipitate separates. Platinum chloride gives no precipitate in dilute solution.

Isoamyl Thiolcarbamate from Isoamyl Thioncarbamate.—Isoamyl thioncarbamate, as prepared in 1853 by M. W. Johnson[1] from "binoxysulphocarbonate of amyl" and ammonia was an oil. Our material also was obtained as an oil which refused to solidify on cooling. When heated (10 grams) with isoamyl iodide (5 grams) at 120°–130° for several hours, it was transformed slowly and less completely than the lower members of this series. The product, crystallized from hot water, formed extremely large, silver-white plates resembling thin slices of mica. It melted at 112°–113°, while Schöne[2] says that isoamyl thiolcarbamate forms plates melting at 107°, when prepared from the chloride $C_5H_{11}SCOCl$ and ammonia. A nitrogen determination gave:

[1] Quart. J. Chem. Soc., **5**, 142. [2] J. prakt. Chem. [2], **32**, 247.

	Calculated for $H_2NCO.SC_5H_{11}$.	Found.
N	9.52	9.16

Isoamyl thiolcarbamate does not differ in properties from the other members of the series. With silver nitrate, mercuric chloride, copper sulphate, etc., it behaves precisely like isobutyl thiolcarbamate.

Ethyl Thioncarbamate and Ethylene Bromide.—When 10 grams of the former and 37 grams of the latter were mixed, and heated on the steam-bath for three hours, ethyl bromide was evolved and, on cooling, a crystalline mass was deposited. It was purified by boiling with alcohol and water, which extracts ethyl carbamate, and was thus obtained as a crystalline powder which was quite difficultly soluble in the ordinary solvents. It was free from bromine, and a nitrogen determination gave the following :

	Calculated for $C_4H_8S_2N_2O_2$.	Found.
N	15.55	14.99

Ethyl Benzenesulphinate, $C_6H_5SO.OC_2H_5$, *with Methyl and Ethyl Iodides.*—The following negative experiments were performed by Mr. T. B. Johnson, to whom we wish to express our thanks. 4 grams of the ethyl ester were heated with 3.6 grams of ethyl iodide at 100°–110° for one hour, when no apparent reaction took place. On further heating, the material darkened but it deposited no crystals when placed in a freezing mixture. Heated further for four hours at 130°–140° considerable decomposition took place. The material, extracted with ether, washed with sodium hydroxide, dried, and evaporated, gave no solid material.

Ten grams of the ester were heated with 8.3 grams methyl iodide for one hour at 110°–120°, then again at 145°–155°. On opening the tube there was much pressure and a thick black oil resulted. This was extracted with ether and washed with sodium hydroxide. On evaporation, 2.5 grams of black oil was obtained which refused to solidify and when heated began to boil at 100° ; then the temperature rose to 250°, when the remaining material charred. Ethyl phenyl sulphone boils unaltered above 300°, and melts at 42°. Methyl phenylsulphone melts at 88°.

NEW HAVEN. CONN., May, 1899.

Contributions from the Chemical Laboratory of Cornell University.

DIMETHYLDIANTHRACENE: A POLYMERIC MODIFICATION OF β-METHYLANTHRACENE.

By W. R. Orndorff and H. A. Megraw.

In a previous paper[1] by one of us it was shown that anthracene, when suspended in benzene and exposed to the sunlight, was rapidly polymerized to a compound having the same percentage composition as the original product but twice the molecular weight. For this product we suggested the name dianthracene instead of paranthracene, as more exact and more scientific. Attempts to prepare derivatives of dianthracene by treating this substance directly with various reagents were unsuccessful, as the polymer was changed into the simple substance, anthracene, under these conditions, and derivatives of anthracene itself were always obtained. We then tried to prepare substitution-products of dianthracene by subjecting derivatives of anthracene to the action of the sunlight. In this way we succeeded in making dihydroxydianthracene (dianthranol)[2] from anthranol (γ-hydroxyanthracene). We further found that when both of the γ-hydrogen atoms were replaced by chlorine, the substance, dichloranthracene $\left(C_6H_4\begin{array}{c}CCl\\|\\CCl\end{array}C_6H_4\right)$, was no longer polymerized by the action of the sunlight.

It seemed to us highly probable that the α- and β-derivatives of anthracene would polymerize in the same way that anthracene itself does since both these derivatives contain the same meso groups, the change in which we found to be the cause of the polymerization in the case of that hydrocarbon. In this way it seemed possible to prepare substitution-products of dianthracene.

The first substance studied was β-methylanthracene, which we found underwent polymerization in the sunlight just as readily as anthracene, forming a compound with the same percentage composition but twice the molecular weight of

[1] This Journal, 17, 658. [2] *Ibid.*, 18, 453.

methylanthracene and which we have, therefore, named dimethyldianthracene.

β-Methylanthracene, $C_{15}H_{12}$, was first obtained by Weiler[1] and O. Fischer,[2] in 1874, by conducting the vapors of dimethylphenylmethane and dimethylphenylethane through a red-hot tube. G. Schultz[3] then found the hydrocarbon among the products formed by heating the oil of turpentine to a comparatively high temperature. Schultz suggested that the compound would be found in coal-tar, and later, working together with Japp,[4] he succeeded in isolating this hydrocarbon from that complex mixture. Wackendorff and Zincke[5] then showed that it is formed in the decomposition of high boiling aniline oils. Nietzke[6] made the substance by heating methyl quinizarin, $\left(C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}C_6H\begin{<}\begin{matrix}OH\ (1)\\CH_3\ (2)\\OH\ (4)\end{matrix}\right)$, with zinc dust, thus showing that it was a β-compound. Later this same β-methylanthracene was also shown to result from the distillation of several plant substances, such as emodin, chrysophanic acid,[7] abietinic acid,[8] and crysarobin[9] with zinc dust. The constitution of this hydrocarbon is determined from its formation[10] from methyl quinizarin by heating this substance with zinc dust. As the methyl quinizarin results from heating phthalic anhydride and hydrotoluquinone together in the presence of sulphuric acid in accordance with this equation:

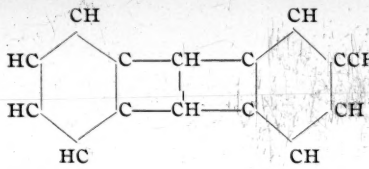
$$C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}O + C_6H_3\begin{<}\begin{matrix}OH\ (1)\\CH_3\ (2)\\OH\ (4)\end{matrix} =$$

$$C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\begin{>}C_6H\begin{<}\begin{matrix}OH\ (1)\\CH_3\ (2)\\OH\ (4)\end{matrix} + H_2O,$$

its constitution is known. The synthesis of methylanthra-

[1] Ber. d. chem. Ges., **7**, 1185.
[2] *Ibid.*, **7**, 1195.
[3] *Ibid.*, **10**, 117.
[4] *Ibid.*, **10**, 1049.
[5] *Ibid.*, **10**, 1485.
[6] *Ibid.*, **10**, 2013.
[7] Liebermann: Ann. Chem. (Liebig), **183**, 163; **163**, 169.
[8] Ciamician: Ber. d. chem. Ges., **11**, 273.
[9] Liebermann and Seidler: Ann. Chem. (Liebig), **212**, 34; Ber. d. chem. Ges., **11**, 1605.
[10] Ber. d. chem. Ges., **10**, 2013.

cene from *p*-xylyl phenyl ketone, $C_6H_5COC_6H_3(CH_3)_2$, accomplished by Elbs and Larsen[1] also leads to the same conclusion, that the methylanthracene is the *β*-compound and has the following constitution:



This *β*-methylanthracene is described as crystallizing in yellow plates (which, however, are perfectly white when pure and show a bluish fluorescence), melting at 199°–200° C. and boiling above 360° C. It is but slightly soluble in alcohol, ether, and glacial acetic acid, though readily soluble in carbon bisulphide and benzene. With picric acid it combines to form a characteristic compound crystallizing in red needles and resembling the anthracene compound with picric acid very closely. The action of sunlight on *β*-methylanthracene has, so far as we are aware, never been investigated.

The product with which we started was purchased from Schuchardt and presumably was obtained from coal-tar. It had the melting-point and all the other properties characteristic of *β*-methylanthracene. When suspended in benzene in white glass bottles and exposed to the action of the sunlight during the summer of 1897 it was rapidly polymerized, forming a white crystalline substance which, when recrystallized several times from toluene, was found to melt with slight decomposition at 228°–230° C. The melting-point of this slightly decomposed product was 200° C. (the melting-point of *β*-methyl anthracene). From this it seemed highly probable that *β*-methylanthracene suffers a similar change in the sunlight to that which anthracene itself undergoes, and moreover that the polymeric product when heated to its melting-point is reconverted into the simple substance from which it was formed exactly as in the case of dianthracene. A con-

[1] Ber. d. chem. Ges., 17, 2849. See also in this connection Hammerschlag: *Ibid.*, 11, 82.

siderable quantity of the polymeric product was now made by the method used in the preparation of dianthracene. It was then purified by boiling with alcohol, acetic acid, and benzene, to remove any substances soluble in these liquids, and by recrystallizing the product, thus purified, four times from toluene. The products of the different crystallizations were checked by combustion analyses. Many analyses were made but a pure product was obtained only after four recrystallizations from toluene. The following are the results of the last four analyses made with this product:

I. 0.2145 gram substance gave 0.7387 gram CO_2 and 0.1183 gram H_2O.

II. 0.1610 gram substance gave 0.5536 gram CO_2, and 0.0909 gram H_2O.

III. 0.2156 gram substance gave 0.7398 gram CO_2, and 0.1184 gram H_2O.

IV. 0.1611 gram substance gave 0.5537 gram CO_2, and 0.0908 gram H_2O.

	Calculated for		Found.			
	$C_{15}H_{12}$.	$C_{14}H_{10}$.	I.	II.	III.	IV.
C	93.75	94.38	93.92	93.78	93.58	93.74
H	6.25	5.62	6.13	6.27	6.10	6.26
	100.00	100.00	100.05	100.05	99.68	100.00

These results show that the product formed by the action of sunlight on solutions of β-methylanthracene in benzene has the same percentage composition as β-methylanthracene itself.

Molecular weight determinations were then made with the pure product, using the boiling-point method and toluene and pyridine as solvents. In making these determinations we used the boiling-point apparatus devised by Orndorff and Cameron,[1] and followed closely the directions given by them. The following are the results obtained:

Molecular Weight Determinations.

β-Methylanthracene, $C_{15}H_{12} = 192$; dimethyldianthracene, $C_{30}H_{24} = 384$. Solvent: toluene, boiling-point 109°.7 at 741.7 mm. Molecular rise for 100 grams 35.1.°

[1] This JOURNAL, 17, 517.

Solvent. Grams.	Substance. Grams.	Observed rise.	Molecular weight found.
83.88	0.5238	0.054°	404
	0.9244	0.089°	433
	2.0109	0.189°	445
	2.3805	0.229°	434
	2.8347	0.271°	437
	Average of five determinations		431
Barometer constant.			
Molecular weight at infinite dilution			387

A second series in toluene gave the following results:

Solvent. Grams.	Substance. Grams.	Observed rise.	Molecular weight found.
99.08	0.4340	0.042°	366
	0.9521	0.083°	406
	1.4011	0.123°	403
	1.8997	0.167°	359
	2.5663	0.216°	421
	Average of five determinations		391
Barometer constant.			
Molecular weight at infinite dilution			390

With pyridine the following results were obtained:

Solvent: pyridine. Boiling-point 114.2° at 741.7 mm. Molecular rise for 100 grams, 26.9°.

Solvent. Grams.	Substance. Grams.	Observed rise.	Molecular weight found.
117.1	0.3242	0.020°	371
	0.6511	0.033°	452
	0.9749	0.051°	438
	1.2941	0.070°	424
	1.5051	0.081°	425
	Average of five determinations		422

These results show that the substance has the molecular weight 384, or twice that of β-methylanthracene, and that it is hence dimethyldianthracene.

The pure product is a white crystalline substance which melts with slight decomposition at 228°–230° (uncorr.) or even lower when the heating is prolonged at the lower temperature. The slightly decomposed product resulting was found to melt at 200° C. (the melting-point of β-methylanthracene),

and to be β-methylanthracene, as it gave with picric acid a compound crystallizing in dark-red needles and melting at 199° C., identical with the β-methylanthracene picric acid compound. The product is therefore a polymer of β-methylanthracene and is changed into this substance when heated to its melting-point. This transformation can be accomplished at a much lower temperature than the melting-point of the polymeric product (228°–230° C.), in boiling liquids in which it is soluble, for example, in anisol, which boils at 155° C., and to some extent in boiling metaxylene (139° C.).

Pure dimethyl dianthracene shows none of the bluish fluorescence so characteristic of pure anthracene and β-methylanthracene. With picric acid it forms no compound. It was not found possible to obtain either β-methylanthracene or dimethyldianthracene in the form of crystals large enough to measure and determine the system; but from its optical properties dimethyldianthracene is either orthorhombic or monoclinic, more probably orthorhombic, while β-methylanthracene is probably monoclinic. Dimethyldianthracene is almost insoluble in all solvents in the cold, and even at the boiling temperature it is but slightly soluble in alcohol, ether, acetone, acetic ether, carbon disulphide, and chloroform. In benzene, toluene, and xylene, at their respective boiling-points, it is somewhat more soluble, the solubility increasing with the boiling-point of the solvent. There are several plant substances, such as emodin, chrysophanic acid, and chrysarobin, which, when distilled with zinc dust, give β-methylanthracene. As these substances are formed in the direct sunlight and undoubtedly contain a residue of β-methylanthracene it is quite possible that they may be derivatives of dimethyldianthracene. Further work will be undertaken in this laboratory to see if derivatives of dimethyldianthracene exists in nature and also to prepare further derivatives of dianthracene.

CORNELL UNIVERSITY, May, 1899.

THE ACTION OF CHROMIC ACID ON HYDROGEN.

By Chas. L. Reese.

In 1872 E. Ludwig[1] published an article on the action of chromic acid on carbon monoxide, hydrogen, marsh-gas, and ethylene, in which he described experiments from which he drew the conclusion that hydrogen is oxidized by a saturated solution of chromic acid under ordinary conditions.

He saturated gypsum balls with a saturated water solution of pure chromic acid and placed these in an atmosphere of hydrogen in tubes over mercury. He gives the figures from one experiment in which 35.8 cc. of gas were completely absorbed in eighty-six hours at 17°–18° C. This article is quoted in a number of reference works as authority for the statement that hydrogen is oxidized by chromic acid.

I repeated Ludwig's experiment a number of times, using not only gypsum but also porous burnt clay balls, and in each case confirmed his results, with this exception, that in no case was all of the hydrogen absorbed, and in the case of the clay balls a much smaller volume was absorbed than in the case of gypsum, some of them having been allowed to stand fifteen to twenty days without showing any change of volume after the first few days.

The chromic acid in the balls was shown to be partly reduced, by the greenish-brown solution obtained from them in water after the reaction. This reduction of chromic acid by hydrogen, however, took place in the presence of a porous material which is known in many cases to aid reaction, and I found in later experiments that the reaction would also take place at the temperature of the room by agitating pure chromic acid solution with hydrogen in sealed tubes containing platinum asbestos, although it would not act in the presence of platinum foil.

When sulphuric acid was added to the chromic acid solution in presence of platinum asbestos the absorption of hy-

[1] Ann. Chem. (Liebig), **162**, 47.

drogen took place much more rapidly, as would be expected.

To determine whether hydrogen was oxidized at all by a saturated solution of pure chromic acid, I at first used graduated gas-measuring tubes with stop-cocks at both ends, the tubes being first filled with the solution and the gas introduced, by displacement, from an electric generator, such as described by Magruder,[1] but these proved unsatisfactory, owing to the action of chromic acid on the grease in the stop-cocks, so that glass tubes were substituted, with capillaries drawn on both ends, which could be sealed and opened without loss of gas. They were filled with the solution and, after the introduction, through capillary rubber connections, of a measured volume of hydrogen from a Hempel burette, were then sealed, the height of the liquid on the tube, under atmospheric condition, being first marked.

A number of these tubes were agitated for from five to fifteen days, by fastening them, by means of clamps which held them at right angles to a revolving shaft which was caused to turn at a rate sufficient to throw the liquid from one end of the tube to the other twice on every revolution.

Pure chromic acid, free from sulphuric and nitric acids was used in some cases and in others concentrated sulphuric acid was added in quantities equal to 1, 2, 5 to 15 per cent by volume; but in no case was the volume of hydrogen found to be changed on opening the tubes, and on analysis the gas was invariably found to be pure hydrogen. It will thus be seen that pure hydrogen is not acted upon by either pure chromic acid solution or one containing sulphuric acid, under ordinary conditions. I next determined to see if the action would not take place at higher temperatures, and for this purpose used tubes similar to those already described except that the chromic acid was introduced into a small bulb containing from 1 to 2 cc. and placed in the tube before the second capillary was drawn out on it. These tubes were then filled with redistilled water and the water displaced by hydrogen, which was measured as before.

The tubes, after the bulbs in them were broken, were at first heated in a Carius furnace to temperatures ranging from

[1] This JOURNAL, 14, 810.

150°–190° C. for from three to five hours, and in every case on opening and analyzing the gas some of the hydrogen was found to have disappeared and more oxygen than enough to make up the difference was found to be present. It was also found that by heating tubes containing air in the place of hydrogen, oxygen was evolved, thus showing that the evolution of oxygen was simply due to the decomposition of the chromic acid in water rather than to the influence of the hydrogen. Having found that hydrogen is oxidized by chromic acid at the above temperatures, I determined to find out, if possible, at what temperature the reaction begins and at what temperature a saturated solution of chromic acid begins to give up oxygen, and whether these two points are identical; that is, whether hydrogen is not acted upon by chromic acid till the latter begins to decompose by heat.

The Carius furnace being unsuitable for constant temperatures I devised another arrangement, which proved very satisfactory. I had cylinders made of 2-inch wrought-iron pipe with a plug forged into one end and a threaded cap fitted on the other, which was rendered vapor-tight by suitable washers, and had holes bored through for thermometer and condensing tube. These cylinders were placed in an inclined position with enough liquid in them of the proper boiling-point to insure their being filled with the vapor when boiled. The tubes were placed in the cylinders and kept separated from the sides by wire or glass triangular supports. The cylinders were covered with sufficient asbestos to prevent radiation and protected from air draughts. With these cylinders it was possible to maintain a constant temperature, just as is done with the Victor Meyer constant temperature bath.

Tubes containing saturated solutions of chromic acid and hydrogen were heated to temperatures ranging from 35°–156° C., the time of heating ranging from five hours for the highest temperature to five hundred hours for the lowest. It will be seen from the accompanying table (I) that there is no evo-

Table I.

	Temperature.	Time in hours.	Hydrogen used. cc.	Hydrogen absorbed. cc.	Oxygen evolved. cc.
1	156°	5	40.6	1.8	7.4
2	"	7	36.0	3.8	19.4
3	138°	7	36.4	3.6	11.8
4	"	6.5	32.7	3.0	6.2
5	135°	8.5	32.2	3.7	5.2
6	111°	5.5	37.4	0.6	0.6
7	"	10	39.6	1.0	1.0
8	100°	16	39.4	0.94	0.6
9	"	25	29.8	9.5	1.2
10	"	60	23.4	22.9	0.6
11	"	116	35.8	25.5	3.7
12	78°	13.5	41.4	0.0	0.0
13	"	25	31.8	0.7	0.0
14	"	25	31.6	0.0	0.0
15	"	32	41.2	2.0	1.7
16	"	60	30.9	5.5	0.5
17	"	90	30.8	2.0	0.8
18	"	120	34.7	7.4	0.7
19	61°	126	39.9	6.5	0.0
20	50°	192	32.1	0.7	0.0
21	"	288	31.0	0.5	0.0
22	40°	260	42.0	0.0	0.0
23	"	240	42.3	0.4	0.0
24	35°	360	42.0	0.0	0.0
25	"	500	44.5	0.2	0.0

lution of oxygen at temperatures below 78° and only in one case, at temperatures below 100°, was the quantity of oxygen very considerable even when heated as long as one hundred and twenty hours. The absorption or oxidation of hydrogen was very considerable at temperatures at and above 61° when heated for a sufficient length of time; but at 50° the absorption was very slight for as much as two hundred and eighty-eight hours heating, and at 40° and below there was no appreciable absorption.

From the results of these experiments I think I can safely say that hydrogen is not oxidized by saturated solutions of chromic acid at temperatures below 50° and that the action is extremely slow below 100°.

The oxygen evolved was measured by absorption in sodium

pyrogallate in a Hempel apparatus. All the volumes given are reduced to normal conditions.

In the experiments at 35° the tubes were agitated as in the earlier experiments, on a revolving shaft in a constant temperature air-bath.

Table II shows the results of heating a number of tubes

Table II.

	Temperature.	Time in hours.	Oxygen evolved.
		cc.	cc.
1	156°	5	19.0
2	119°	4.5	9.7
3	111°	11	0.3
4	100°	15	0.3
5	"	25	1.3
6	"	30	0.6
7	"	60	1.3
8	78°	135	0.0
9	"	129	0.7

containing air in the place of hydrogen, to determine at what temperature a saturated solution of chromic acid would give up oxygen. These experiments show that such a solution decomposes quite rapidly at temperatures above 119°, and very slowly, indeed, at lower temperatures, ceasing altogether at 78°.

As hydrogen is oxidized at temperatures below those at which oxygen is given off by chromic acid, the oxidation of hydrogen does not seem to be dependent upon the decomposition of chromic acid by heat, in fact at higher temperatures a large excess of oxygen was evolved, above the equivalent of the hydrogen oxidized, while some hydrogen still remained.

It is interesting in this connection to note that Berthelot[1] found that hydrogen is not oxidized by nitric acid at 100°, although nitric acid gives up oxygen at this temperature.

Action of Electrolytic Hydrogen.

I next turned my attention to the action of hydrogen produced electrolytically in a solution of chromic acid. For this purpose a normal solution of chromic acid was used because it could be more readily titrated to determine the amount of

[1] Compt. rend., **127**, 27–29.

reduction. The solution was placed in a burette and platinum electrodes were used, the connections passing through glass tubes into which the electrodes were sealed. The hydrogen electrode was placed at the bottom and the other at the top of the liquid so that the hydrogen gas could pass up through the liquid and the oxygen pass out at the top. Any product of reduction being heavy would remain near the bottom, as was found to be the case in certain solutions, and thus escape oxidation. When the amount of reduction was studied the solution was well mixed from time to time. The long narrow tube was used to prevent spattering and loss by evaporation, and the burette form was used so that the solution could be drawn off from time to time, well mixed, and a portion titrated, the rest being returned to the tube for the purpose of continuing the experiment. The current used was from two storage battery cells so that there was an abundant evolution of hydrogen.

Perfectly pure chromic acid free from any trace of sulphuric acid was not reduced at all after passing the current through for twenty-four hours ; but if it contained the slightest trace of sulphuric acid or a sulphate, reduction took place as was seen in a few minutes from the darkening of the solution and the absorption of the hydrogen ; but there was always a limit reached when no further reduction took place. In the case of a specimen containing a trace of sulphuric acid the reduction was complete after 2.85 per cent had been reduced, although the current was allowed to act for two days after this point had been reached.

Sulphuric acid, potassium sulphate, and chromium sulphate were added to the pure chromic acid solution and in each case reduction took place up to a definite percentage and then stopped. Pure potassium bichromate was not reduced at all, but on addition of sulphuric acid or a sulphate, reduction took place in the same way as with the pure chromic acid to which these substances were added.

The fact that a limit is reached in the electrolytic reduction of chromic acid containing definite quantities of sulphuric acid or a sulphate may lead to a means of determining the quantities of these substances present in a specimen of

chromic acid or to a means of determining the relative strength of the two acids. Sufficient data, however, have not yet been obtained for determining this question.

The titrations in these experiments were carried out by reducing the acid with ferrous ammonium sulphate and titrating back with potassium permanganate. The green color of the chromium sulphate does not interfere at all with the end reaction. The method is perfectly reliable as I have compared it with Bunsen's method as well as with the gravimetric method.

The chromic anhydride used in these experiments was obtained from Gehe & Co., of Dresden, and was marked "free from sulphuric acid." One lot of it did not show a trace of sulphuric acid and was extremely pure. I have been able to recrystallize this acid by allowing a saturated water solution of it to stand in a desiccator over calcium chloride. It crystallized in beautiful solid rosettes which appeared almost black by reflected light and a beautiful ruby color by transmitted light. It was suggested that these crystals might be the hitherto unobtained chromic acid, but on analysis they proved to be the anhydride.

JOHNS HOPKINS UNIVERSITY,
May, 1899.

Contributions from the Chemical Laboratory of Purdue University.

ACTION OF SULPHURIC ACID ON NITROHEPTANE.

BY R. A. WORSTALL.

The nitrosulphonic acids constitute a class of compounds practically unknown in the aliphatic series. For while these derivatives are readily obtainable in the aromatic series by nitration of sulphonic acids or by sulphonation of nitro hydrocarbons, no corresponding reactions are known in the case of paraffins.

Victor Meyer[1] has shown that the action of fuming sulphuric acid upon nitroethane gives ethylene disulphonic acid, while

[1] Ann. Chem. (Liebig), 171, 53.

concentrated sulphuric acid gives acetic acid as the chief product. In the latter case, however, upon neutralizing the sulphuric acid solution with barium carbonate, he also obtained a barium salt containing nitrogen, but in such minute quantity that he was unable to identify it, although he suspected that it was the salt of a nitrosulphonic acid.[1] Having on hand a small quantity of nitroheptane a study of its reactions with sulphuric acid of different degrees of concentration was undertaken, with the hope of obtaining a nitrosulphonic acid.

Action of Dilute Sulphuric Acid.

Five grams of nitroheptane (boiling-point 193°–196°) were digested with 50 grams of dilute sulphuric acid (1 part acid to 5 parts water) at about 80° for ten minutes. The solution was cooled, diluted, and extracted with ether. The ether was removed by evaporation. There was a residue (5 grams) with the characteristic odor of the fatty acids. This residue was boiled with water and calcium carbonate, the solution filtered, and silver nitrate added to the filtrate. A white flocculent precipitate was formed. This silver salt was washed, dried, and analyzed.

0.2012 gram gave 0.0923 gram Ag.

	Calculated for $C_7H_{13}O_2Ag$.	Found.
Ag	45.6	45.8

The product of the reaction was therefore heptoic acid, formed as follows:

$$C_6H_{13}CH_2NO_2 + H_2O = C_6H_{13}COOH + NH_3O.$$

Action of Concentrated Sulphuric Acid.

Five grams of nitroheptane were gradually added to an excess of concentrated sulphuric acid (specific gravity 1.84). A reaction took place at once with the evolution of heat. The solution was diluted and extracted twice with ether. The ether was removed from the extract by evaporation and the residue converted into the silver salt in the usual manner. The latter was analyzed.

0.0824 gram gave 0.0380 gram Ag.

[1] Ann. Chem. (Liebig), 171, 54.

	Calculated for $C_7H_{13}O_2Ag$.	Found.
Ag	45.6	46.1

The sulphuric acid solution which had been twice extracted with ether still retained a yellow color. It was neutralized with barium carbonate, filtered, and the filtrate evaporated to dryness. A small quantity of a yellow salt remained which contained no nitrogen, and was found to be the barium salt of heptoic acid. The action of concentrated sulphuric acid, therefore, is the same as that of the dilute.

Action of Fuming Sulphuric Acid.

Ten grams of nitroheptane were gradually added with constant shaking, to 50 grams of fuming sulphuric acid, kept cold. Some sulphur dioxide was liberated, and upon diluting with water a small quantity of a carbonized residue remained insoluble. Upon allowing the diluted solution to stand, a fatty acid separated as an oil at the top. The solution was repeatedly extracted with ether, the ethereal solution evaporated, and the silver salt of the residue, which amounted to 4 grams, was formed in the usual manner. This silver salt was analyzed.

0.1030 gram gave 0.0465 gram Ag.

	Calculated for $C_7H_{13}O_2Ag$.	Found.
Ag	45.6	45.1

The acid solution left after the extraction with ether was neutralized with barium carbonate, and filtered. The yellow solution thus obtained was evaporated to dryness, leaving as a residue 2 grams of a brown barium salt. Qualitative tests showed the presence of sulphur and of nitrogen. This salt was extracted with boiling 90 per cent alcohol, filtered, and the solution evaporated to a small volume. Upon long standing, small reddish-yellow plates crystallized out. These were removed, dried, and analyzed.

0.1506 gram gave 0.0614 gram $BaSO_4$ (for barium).

0.2175 gram gave 0.1602 gram $BaSO_4$ (for sulphur).

0.1114 gram gave 4.6 cc. nitrogen at 742 mm. and 18°.

	Calculated for $(C_7H_{14}<^{SO_3}_{NO_2})_2B$	Found.
Ba	23.42	23.97
S	10.94	10.37
N	4.74	4.62

The compound was therefore undoubtedly the barium salt of nitroheptanesulphonic acid. This salt was readily soluble in water and in hot alcohol, differing in the latter respect from barium heptylsulphonate.[1] It crystallized poorly from alcohol in small plates. In all, but 1 gram of the purified salt was obtained from 10 grams of nitroheptane—a yield of but 5 per cent of the theoretical.

Twenty grams of nitroheptane, when sulphonated in the same way, yielded two grams of the barium salt. This was dissolved in water, the barium precipitated with dilute sulphuric acid, the solution filtered, neutralized with lead carbonate, and filtered again. The lead was removed by means of hydrogen sulphide, and the filtrate evaporated to dryness. A small quantity of a thick, brown syrup remained, which could not be purified for analysis.

It is to be regretted that a better yield could not be obtained in order that other reactions might be tried for identification. But it is believed that the method of formation, together with the analysis and properties of the barium salt, afford definite proof of the formation of a nitrosulphonic acid. While there is no proof to that effect, it would seem probable that in the sulphonation of a nitroparaffin, the same law would hold good as in the case of the sulphonation of other substituted paraffins—that is, that the sulphonic acid group attaches itself to the carbon atom adjacent to the one which carries the substituting radical. An attempt was made to prepare a sulphonic acid by acting upon bromnitroheptane, $C_6H_{13}CHBrNO_2$, with sodium sulphite, but without success, as ammonia was evolved each time. The formation of this nitrosulphonic acid is interesting in that it shows another reaction possible in the aliphatic as well as in the aromatic series.

LAFAYETTE, IND., March, 1899.

[1] This JOURNAL, **20**, 669.

REVIEWS.

CHEMICAL EXPERIMENTS. By J. F. WOODHULL, Professor of Physical Science, Teachers' College, Columbia College, New York, and M. B. VAN ARSDALE, Instructor in Physical Science in Horace Mann School and Assistant in Teachers' College. New York: Henry Holt & Co. 1899.

On examining this book one is struck with several features which are, unfortunately, not usually found in books of this kind, the principal one being its simplicity. The great amount of material and bewildering mass of details so often found are omitted here; but a few of the elements, and their relation to important processes and substances, are studied, and the broad bearing of the subject developed by suitable questions. An idea of the method can be obtained by a brief summary of the first few experiments. After making oxygen, attention is drawn to its power to support combustion, its presence in air, relation between pure oxygen and air, rusting and its causes, and combustion in general, with the methods of testing and proving these facts, and some general broad deductions that can be drawn from a consideration of the phenomena observed. Hydrogen, chlorine, acids, bases, and salts, etc., are likewise treated in a simple, clear way, which with classroom exercises of equal value, cannot fail to awaken the interest of the student in the processes which are constantly in progress in nature. Another noteworthy feature is the extreme simplicity of the apparatus used, such as can be secured for a small sum and readily used where no special facilities for laboratory work are offered. These experiments are only printed on one side of the page, the blank leaf being intended for the records. This book can be used to great advantage in the lower grade schools, in most of which the sciences are now taught. J. E. G.

QUALITATIVE ANALYSIS FOR SECONDARY SCHOOLS. By C. W. IRISH, A.B. (Harvard), Head Master of Lowell High School, Lowell, Mass. American Book Co. 1899. Price, 50 cents.

The author has attempted to prepare a book which can be used by secondary schools, and has introduced the simplest methods possible. The regular system of qualitative analysis, with some omissions of complex methods is adopted, and the principal reactions of each metal are given, and also some questions regarding its occurrence, compounds, etc., with equations representing some of the reactions which are to be filled out and balanced. J. E. G.